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The chemical mechanism generation programme CHEMATA—Part 2: Comparison of four chemical mechanisms for mesoscale calculation of atmospheric pollution

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Abstract

RACM and the three new mechanisms described in the companion paper (the extended, reduced and small mechanisms) are implemented in a mesoscale 3D transport-chemistry model (TAPOM for Transport and Air POllution Model) in order to find an optimum between calculation speed and mechanism detail. The 3D tests are performed in the domains of Milan, Mexico City and Bogota. The three domains present different chemical and meteorological conditions, which are used to test the behaviour of the four mechanisms in different situations. Three emission scenarios are simulated: the whole emission inventory, 35% NO_x reduction and 35% VOC reduction. The comparison of the four mechanisms is performed for O_3, NO_x , aldehydes and peroxy radicals. Only the small mechanism presents significant differences in ozone concentrations. RO_2 and aldehyde differences are important with the reduced and the small mechanism, which share a new RO_2 parameterisation. Compared to RACM, the small mechanism shows very large differences for aldehydes and RO_2. The extended mechanism and RACM show almost the same ozone response to emissions reduction strategies, and the reduced mechanism presents differences in the range of 10% with respect to the extended mechanisms. The small mechanism is found to be the most VOC sensitive and therefore presents very different results from the other when emissions are modified. The results indicate a strong restriction to the use of the small mechanism in 3D models. Finally, the calculation time required for the calculation of a simulation with the four mechanisms is compared.

Keywords: Mesoscale modelling; Tropospheric chemistry; Chemical mechanism generation; VOC lumping; Emissions reduction strategies

1. Introduction

3D air quality models are powerful tools to simulate the chemical processes occurring in the atmosphere. Due to the huge number of chemical species and the complexity of the processes involved, the formation of secondary photochemical pollutants is highly non-linear. The simulation of atmospheric chemistry is calculated by the means of chemical mechanisms, which are simplified representations of the actual atmospheric chemistry. Chemical mechanisms must be detailed enough to take into account all the most important reactions but should not require too much

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calculation time to be suitable for 3D air quality modelling.

3D models can be used for different purposes needing different kinds of chemical mechanisms. For example, emission abatement strategies assessment may require very detailed mechanisms in order to simulate with enough precision, a maximum of chemical species involved in the ozone formation processes, the behaviour of which can vary under different chemical conditions. These detailed mechanisms consume a lot of calculation time. Daily ozone forecasting needs very quick simulation. A less-detailed mechanism is sufficient if it is able to give accurate ozone results, even with less reliable results for other species. The calculation time saved by using a smaller chemical mechanism can be invested in the integration in air quality models of processes other than gaseous chemistry. Aerosol chemistry, heterogeneous reactions, high-resolution calculation or air quality studies in complex terrain, are examples of tasks for which the optimisation of gas phase chemistry mechanisms could save calculation time.

One of the most important features of 3D mesoscale air pollution models is their ability to simulate emission abatement strategies. Investigating the effects of emissions abatement strategies on pollutant concentrations requires numerous simulations with various scenarios of emission reductions (Couach et al., 2004). Since the behaviour of diverse mechanisms might be different when the emissions are decreased, this paper presents a comparative study of the response of four chemical mechanisms to the emissions abatement strategies. Moreover, the differences can vary from one modelling area to another, depending on the emission strengths and meteorological conditions of the simulation domain. Abatement strategies have therefore been performed on three different cities: Milan, Mexico City and Bogota. Three simulations (one with the whole emissions inventory and two with the emissions reduction scenarios) are performed for each simulated city and each chemical mechanism.

The four chemical mechanisms tested are RACM (Stockwell et al., 1997) and the three new mechanisms generated by CHEMATA (called the extended mechanism, the reduced mechanism and the small mechanism) presented in Part I (Kirchner, 2004). All are implemented in the Transport and Air POllution Model (TAPOM), a 3D eulerian air quality model (Martilli et al., 2003; Haurie et al., 2004). The model calculates gas phase chemistry, transport, diffusion, solar radiation and dry deposition. Since TAPOM does not calculate any atmospheric dynamics, the meteorological data are given as input (wind speed, wind direction, temperature, humidity, pressure, air density, turbulent coefficient). The advection is solved with the third-order scheme PPM (parabolic piecewise method) of Collela and Woodward (1984). The meteorological inputs for the simulations in Mexico City and Bogota have been calculated by the mesoscale model described in Martilli et al. (2002a).

2. Description of the simulation domains

Simulations have been performed on the urban areas of Milan (Italy), Mexico City (Mexico) and Bogota (Colombia). These cities lie at different latitudes and longitudes and have different topographical characteristics, which leads to different meteorological conditions. The different numbers of inhabitants and population densities result in different kind of pollutant emissions. As air quality depends mainly on emissions and meteorology, theses differences are used to test the robustness of the different chemical mechanisms.

2.1. Emissions

Mexico City is the second most populated urban area in the world (after Tokyo) with about 20 million inhabitants living on a surface of 1476 km^2 (11,700 inhabitants km^{-2}). The population of Bogota is about 6.8 million inhabitants with a density of 4318 inhabitants km^{-2}. The built-up area of Milan with 5.5 million people has fewer inhabitants than Bogota but the relatively small extent of its urban surface leads to a higher population density (7377 inhabitants km^{-2}). This concentration of population, coupled with the important industrial activity of Milan leads to high levels of emissions. Milan lies on a plain at 100 m above sea level (ASL) while Bogota and Mexico City were built on a high plateaux (2600 and 2200 m ASL, respectively). This high altitude situation, because of the lower atmospheric pressure, increases the CO emission (less O_2 results in poor combustion of gas in car engines) and decreases the NO_x emissions (less N_2).

2.2. Meteorology and the ozone plume

The simulated periods for the three cities correspond to three ozone pollution episodes, which always appear under high solar radiation and low wind conditions. In such situations, the atmospheric circulation is mainly driven by ground heating, which generates upwards slope winds during the day and downwards slope winds during the night.

Milan is located at 100 m ASL in the Po Valley, about 40 km south of the Alps. Because of the ground cooling, the atmosphere is very stable during the night and the wind is very weak in the Po Valley. The ozone precursors emitted by the city accumulate in Milan and its surroundings. After sunrise, the ground

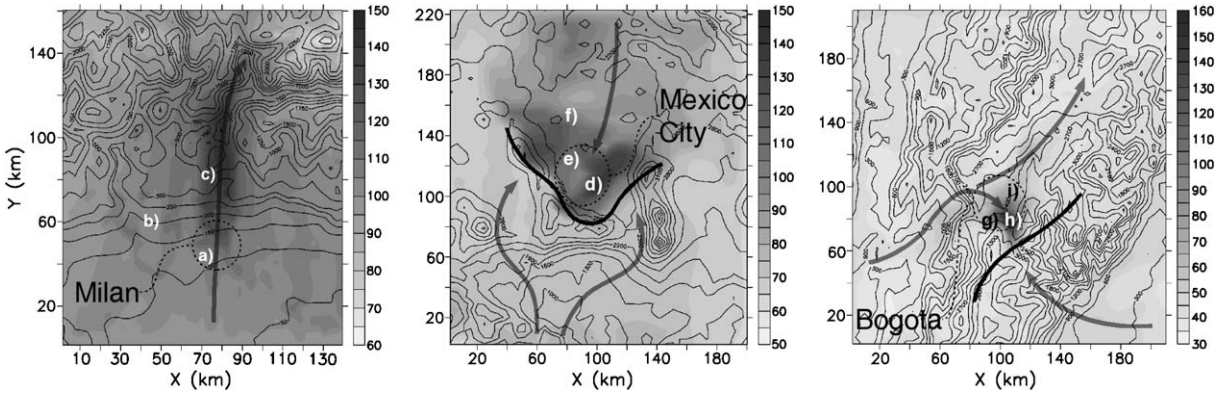

Fig. 1. General air circulation (arrows) and convergence fronts (black lines) in Milan, Mexico City and Bogota. The greyscale background is the ozone concentration (ppb) simulated by RACM at 5 p.m. in Milan, 4 p.m. in Mexico City and 11 a.m. in Bogota. The contour is the topography. The letters locate the measurement stations presented in Fig. 2.

temperature increases, generating slope winds in the Alps and northwards flows in the Po Valley. These winds transport the pollution accumulated in the plain from Milan to the Alps. Simultaneously, the photochemical processes leading to ozone generation take place in the plume and a maximum ozone concentration (172 ppb) is found at 1 p.m. outside the city.

Mexico City and Bogota show some similarities. Both cities lie on high plateaux and are surrounded by mountains. As in Milan, the winds are weak at night and the ozone precursors are accumulated at ground level. During the day, the situation is different than in Milan; slope winds are generated on both sides of the mountains around the cities and flow convergences appear over the urban area. The ozone maxima are found at the convergence fronts where pollutants accumulate (see Fig. 1). In Mexico, the slope winds generate southward and northward flows (Bossert, 1997; Fast and Zhong, 1998). The convergence line is oriented in the west–east direction and appears in the south of the city. In Bogota, the slope winds blow from the west and east of the city and create a rather south–north oriented convergence line (Zarate, 2001–2004). In Mexico and Bogota, the ozone maximum appears at the convergence lines over the cities rather than over the countryside, as in the case of Milan. A major difference between the pollution episode of Mexico and Bogota is that in Mexico, the ozone maximum is reached at 4 p.m, whereas it appears at 11 a.m. in Bogota. The maximum ozone concentrations in Mexico and Bogota calculated using RACM reach 146 and 160 ppb, respectively.

3. Validation of the TAPOM model with RACM

In the three simulation domains, field measurements are available for different pollutants. The simulations of TAPOM with RACM have been compared with O_3 and the available nitrogen oxides (NO_x in Milan and Bogota and NO_2 in Mexico). The comparisons with ozone are presented here. In Milan, the whole set of meteorological data calculated by the Thermal Vorticity Model (TVM) and validated by Martilli et al. (2002b) were given as an input to the TAPOM model. The results from TAPOM, using the RACM chemical mechanism, have been compared to the same measurements and validated using the same methodology: the measurements stations have been classified in three categories, using the average night ozone concentration and the maximum daytime concentration.

In the first category are stations where important NO_x emissions occur. NO_x reacts with ozone during the night, reducing its concentration to zero, see Fig. 2 letter a (letters in Fig. 2 also refer to Fig. 1 where they indicate the locations of each measurement station).

The stations in the third category are far from the sources, in Milan's ozone plume. The night value is rather high because of the low level of emission. The pollution is not produced locally but is transported from the southern urban area (Erba, Fig. 2 letter c). This transport of pollutants finds expression in a narrow, solar radiation-independent ozone peak.

Stations in the second category are between category 1 and 3 (see Varese, Fig. 2 letter b). TAPOM generally succeeded in reproducing the low levels during the night in category 1 sites, and the afternoon's peak of the stations of the third category, although it is slightly underestimated.

In Mexico City, distinguishing between categories is not possible because the plume is not pushed outside the city but is kept over the urban area by the wind convergence. All the presented monitoring stations are located in the city boundaries and show ozone

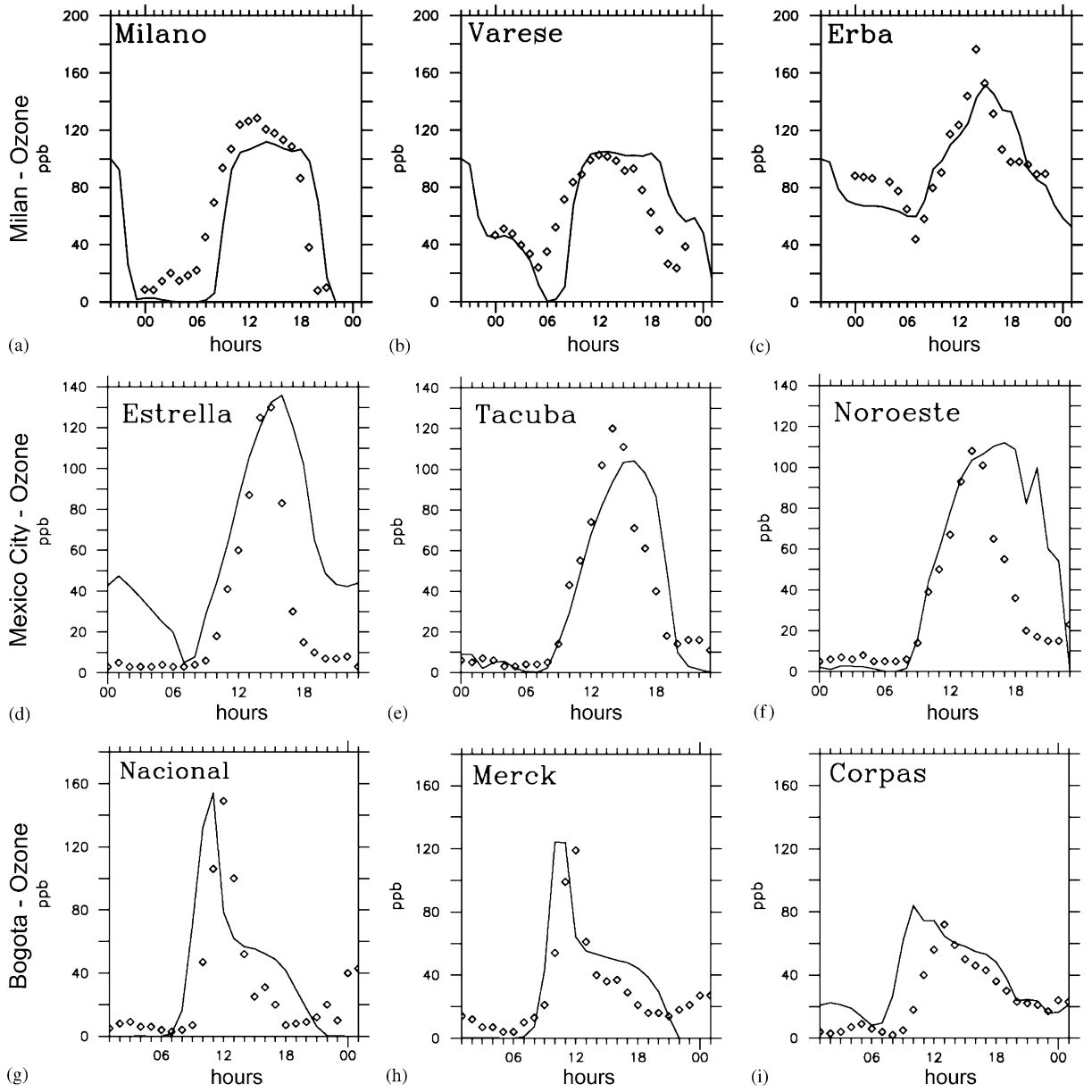

Fig. 2. Comparison of ozone measurements (diamonds) and simulation results (solid line) in Milan, Mexico City and Bogota (in ppb). Simulations have been carried out by TAPOM with RACM. The letters identify the measurements stations in Fig. 1.

concentrations falling to zero at nighttime. But the measured ozone peaks show the same shape as in category 3 in Milan, which denotes transported pollution (Fig. 2, letters d–f). TAPOM succeeds in simulating the increase of the ozone concentration and the peak values in most of the measurement stations. Even though the simulated decrease is not as rapid as the measured decrease, the general behaviour of the ozone concentration is well represented.

Two of the three measurement stations in Bogota are located down town (Fig. 2, letters g and h) and the third is up north in a less urbanised area (Fig. 2, letter i). The measurements in the city show very rapid growth of the ozone concentration and extremely narrow peaks occurring very early. Ozone is therefore very likely to be formed upwind and transported. Outside the city the ozone production is lower and the peak is wider. These different behaviours have been successfully simulated by TAPOM.

4. Comparison with whole emissions inventories

The results are presented as differences with respect to the more detailed mechanism. This allows a comparison of the mechanism's results regarding the number of species. Hence, the following comparisons show the differences between the extended mechanism and the three smaller mechanisms. In order to have a general overview of the comparison of the four mechanisms, the comparisons are made using two criteria:

- The average of the absolute value (AAV) of the differences between the extended mechanism and the other three mechanism is computed by

$$\mathrm{AAV} = \frac{\sum_{i=1,n}|X_i|}{n} \text{ with } X_i = \frac{R_i^{\mathrm{ext}} - R_i^{\mathrm{mech}}}{\overline{R^{\mathrm{ext}}}} \text{ and } \overline{R^{\mathrm{ext}}} = \frac{\sum_{j=1,n} R_j^{\mathrm{ext}}}{n}. \quad (1)$$

R is the calculations' results for the variable of interest (O_3, NO_x etc), "ext" in superscript stands for the simulation with the extended mechanism and "mech" is for RACM, the reduced or the small mechanism. X is therefore the difference between two mechanisms normalised with respect to $\overline{R^{\mathrm{ext}}}$, the average result of the extended mechanism (at ground level, for the whole domain and 24 h: $n = 24\times$ number of cells in x direction $\times$ number of cells in y direction). The use of relative differences allows the comparison of species having different ranges of values, and using the mean result $\overline{R^{\mathrm{ext}}}$ as reference instead of R_i^{ext} (the actual cell value), avoids possible divisions by zero and meaningless high results when dealing with very small values. The mean, computed at ground level for the whole domain and for 24 h, is performed on the absolute value of X in order to prevent the positive and negative differences from neutralising each other.

- The root-mean-square (RMS) of the relative ozone difference between the extended mechanism and the three smaller mechanisms is calculated with the following formula:

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1,n} X_i^2}{n}}, \quad (2)$$

where X_i is the same as in Eq. (1). The RMS is another way to evaluate a mean of differences generating an always-positive result, by squaring the variable. This also gives more importance to values more distant from unity. The RMS calculation is provided for the ozone comparison as double check for the global tendencies of the differences' evolution with respect to the various mechanisms.

4.1. Ozone comparison

4.1.1. Ozone peak

In the three domains, the ozone peaks are not significantly different for the three larger mechanisms, but the peaks generated by the small mechanism are always the largest. In Mexico City and Bogota, the small mechanism produces, respectively, 51% and 56% more ozone than the extended mechanism. Bogota is the only domain where a difference in the time and location of the ozone peak is generated. The peak concentration of ozone generated by the small mechanism appears at 10 a.m. instead of 11 a.m. (Fig. 3), and it is located one cell upwind.

The cell in which the peak occurs in Bogota is inside the urban area with the small mechanism, while with the other mechanisms, the peak is reached an hour later and the air masses are pushed one cell further, out of the city. This explains the difference seen during the night in

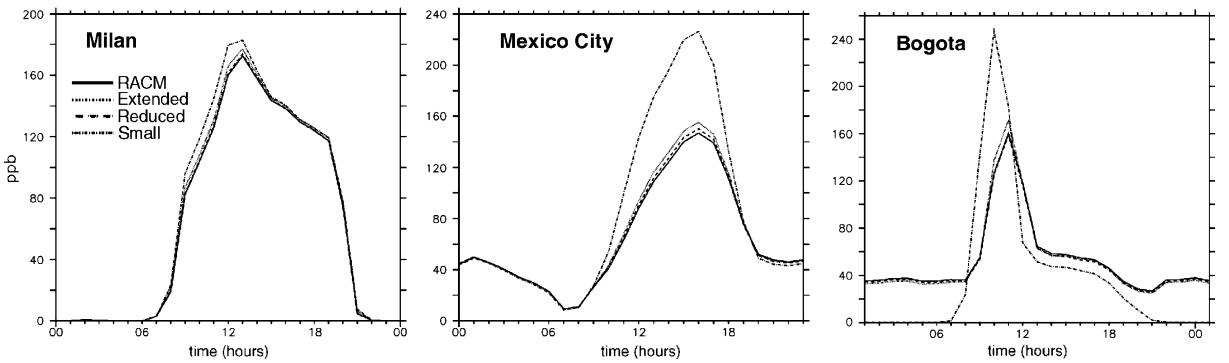

Fig. 3. Time series of the ozone peak in Mexico City, Milan and Bogota for the four mechanisms. The small mechanism always presents a higher peak. In Bogota, the cell in which the peak occurs with the small mechanism is not the same as for the other mechanisms. The figure presents for each mechanism the cell in which the peak occurs.

Fig. 3 for Bogota. The ozone concentration for the small mechanism is zero during the night because of the high level of emissions in the urban cell, and the other three mechanisms show a value of about 30 ppb, which is the background value for this domain.

In Bogota and Mexico City, the small mechanism highly overestimates the ozone peak (by 54% and 55%, respectively). In Milan, the peak is also too high, however, it stays in a reasonable range (5%). As shown in Part I (Kirchner, 2004), the small mechanism produces more ozone in polluted areas (Part I, box model studies, case 2). The difference between the small over estimation in Milan and the cases of Mexico City and Bogota lies in the NO_x or VOC sensitivity of the area in which the peak occurs. The study of the emission reduction scenarios showed that in Mexico City and Bogota, the peak occurs inside a VOC-sensitive region. The higher reactivity of the VOCs in the small mechanism therefore generates very important ozone production. In Milan, the region is NO_x sensitive, which leads to a lower overestimation of the ozone peak.

4.1.2. Relative ozone difference

RACM and the reduced mechanism show very small ozone differences with the extended mechanism, for the three domains (with a maximum of 2.8% for the reduced mechanism in Bogota). This is not the case for the small mechanism, which shows very variable differences between the simulation domains. Although ozone difference for the small mechanism is limited in Milan (1.4%), it exceeds 5% in Mexico City and 25% in Bogota. This very high difference in Bogota can be explained by the evolution of the ozone concentration. In this case, the ozone increase is very rapid and is followed by an almost quick decrease. The peak therefore has a very narrow shape. In Bogota, the small mechanism has indeed simulated narrow peaks but has by far overestimated the ozone maximum and located the ozone peak 1 h early, and hence one cell up wind (as seen in Section 4.1.1). This leads to large differences when comparisons are performed hour-by-hour and cell-by-cell between the small mechanism and the extended mechanism.

The RMS of the relative ozone difference, presented with the AAV in Table 1, is very close to the AAV values. Their values are always a little larger but follow the same pattern.

4.2. Further comparison of NO_x, peroxy radicals and aldehydes

The AAV of the relative differences between the extended and the three other mechanisms are presented in Fig. 4 for four chemical species: O_3, NO_x, RO_2 and ALD. In the following results, RO_2 and ALD stand, respectively, for the sum of all peroxy radicals and aldehyde species in the considered mechanism. The RO_2 differences are presented in order to evaluate the impact of the new parametrisation of the peroxy radicals introduced in the reduced mechanism and the small mechanism. The extended mechanism has a larger number of aldehydes and ketones. ALD will assess the change due to this extension of the mechanism. Ketones are not compared here because the small mechanism does not take them into account and because they are expected to have less effect on ozone due to their lower reactivity.

In the three domains, NO_x shows growing differences from RACM to the small mechanism. Differences are generally under 5% but grow up to 11% with the small mechanism in Bogota. The larger NO_x differences with the small mechanism can also be explained by the larger ALD difference. Higher ALD concentrations lead to higher PAN concentrations, and therefore less free NO_x.

RACM and the reduced mechanism show similar differences for aldehydes and peroxy radicals in the three simulation domains. The small mechanism on the other hand presents larger differences, especially for ALD (up to 56% in Milan for the small mechanism and, respectively, 8% and 13% for RACM and the reduced mechanism).

The calculation of AAV describes the overall differences between two mechanisms but does not indicate which ones are closer to one another. In the city of Bogota, the RO_2 AAV shows almost the same differences for RACM and the reduced mechanism with respect to the extended mechanism. A more precise comparison shows that the extended mechanism produces more RO_2 than RACM but less than the reduced mechanism and the small mechanism. This can

Table 1
AAV and RMS of the differences of ozone between the extended mechanism and the three other mechanisms for the three city cases

	RACM		Reduced mechanism		Small mechanism	
	AAV	RMS	AAV	RMS	AAV	RMS
Mexico city	0.012	0.013	0.008	0.011	0.052	0.085
Milan	0.002	0.003	0.004	0.007	0.014	0.024
Bogota	0.023	0.024	0.028	0.033	0.265	0.279

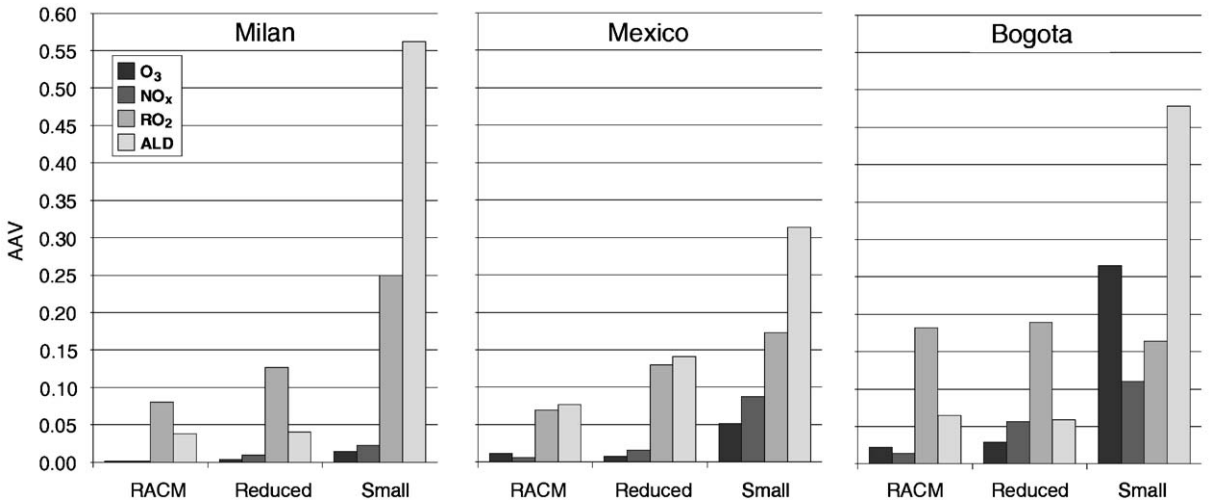

Fig. 4. AAV of the ozone differences between the extended mechanism and the three smaller mechanisms for the different cases.

obviously not be seen in the AAV results because the information is lost in the calculation of the absolute value. The extended mechanism and RACM share the same RO_2 parameterisation.

The extended mechanism produces more RO_2 than RACM because it holds more secondary VOC species, which leads to a higher production of associated peroxy radicals. The other two mechanisms use another parameterisation of RO_2 species that produced a larger amount of RO_2. The small mechanism generates an even larger amount of peroxy radicals than the reduced mechanism because the lumping of its VOC species leads to inaccuracies in the VOCs reactivities. The small mechanism is found to be more reactive.

ALD concentrations are also larger in the extended mechanism than in RACM and even larger in the reduced mechanism and the small mechanism. ALD species are formed from peroxy radicals. With all mechanisms the amount of aldehyde species directly depends on the RO_2 concentration.

5. Comparison with reduced emissions

5.1. Emission reduction with RACM

In order to assess the behaviour of the four mechanisms to emissions reduction, two simulations have been performed, with 35% reduction of the NO_x or VOC emissions. The results of these simulations are presented with plots of the difference in ozone values between the runs with VOC and NO_x emissions reductions (O_3 produced with 65% VOC–O_3 produced with 65% NO_x, hereafter referred to as ΔO_3). Two regions show up in these plots: if ΔO_3 is positive, the NO_x reduction is more efficient and the region is called NO_x sensitive. If the VOC reduction is more efficient, ΔO_3 is negative and the area is named VOC sensitive.

In each case, regions of high NO_x emission concentration, as in the city centres, are VOC sensitive. During the day, the plume generally moves out of urban areas to regions of less NO_x emissions and the sensitivity switches to NO_x sensitive (Couach et al., 2004; Martilli et al., 2002b).

In Mexico City, NO_x-sensitive regions appear at 12 a.m. on the northeast of the urban area, growing until 4 p.m. (see Fig. 5). The city centre remains VOC sensitive all day long.

In Milan, all the built-up area surrounding the city is VOC sensitive until 12 a.m. From 1 to 5 p.m., almost all the domain becomes NO_x sensitive, except Milan itself which remains slightly VOC sensitive. After 5 p.m., the city and its surroundings progressively become more VOC sensitive. The most significant effect of the NO_x emission reduction is seen in the ozone plume, but it is less important than for both of the other cities (Fig. 5). In Bogota, the only VOC-sensitive region is the very centre of the city, from 8 to 10 a.m. (Fig. 5). Afterwards, the plume is NO_x sensitive. Outside the city, the domain is rather insensitive to NO_x or VOC emissions reduction.

5.2. Emission reduction for the four mechanisms

The reduction of the emissions points out the two chemical regimes that drive the production of O_3. To compare the sensitivity of the chemical mechanisms to

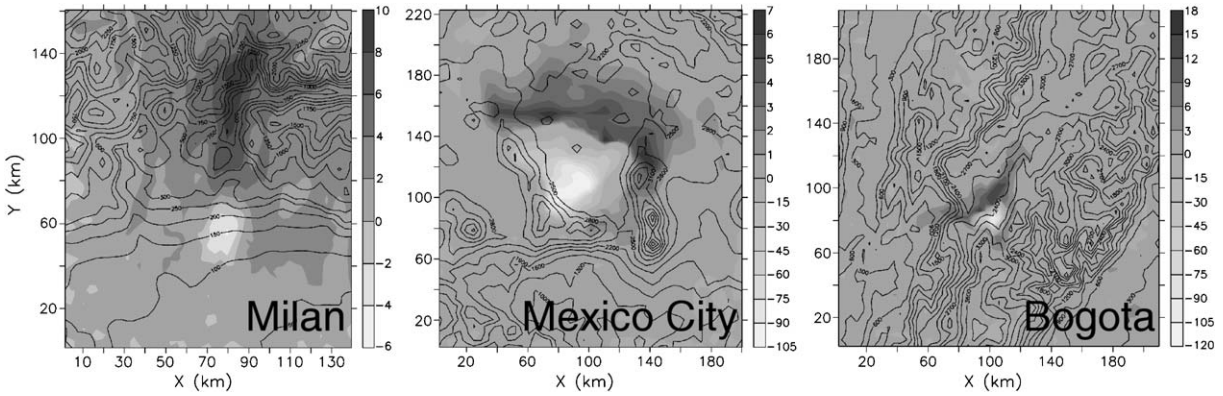

Fig. 5. Differences of ozone concentrations simulated by RACM between the runs with 35% reductions of VOC and NO_x emissions (ΔO_3, in ppb) for the three simulation domains (Mexico City: 4 p.m., Milan: 6 p.m. and Bogota: 10 a.m.). In the negative areas (light greys), a reduction of the VOC emissions is more efficient on the ozone reduction (VOC-sensitive regions), and the positive areas (dark greys) are NO_x sensitive.

emission reduction, the following comparisons are performed:

- *The AAV of the ΔO_3 differences between the four mechanisms* gives a general understanding of the differences generated by the mechanisms when the chemical mechanism is changed (see Section 5.1 for the definition of ΔO_3).
- *The cumulated surface of the NO_x-sensitive area* defines a more precise parameter on the ozone production sensitivity for each mechanism.

5.2.1. The AAV of the ΔO_3 differences between the four mechanisms

As described in Section 5.1, ΔO_3 shows the sensitivity of ozone production to a reduction of NO_x or VOC emissions. A small ΔO_3 difference between the extended mechanism and a smaller mechanism denotes a similar response to emissions reduction. The average of the absolute value of this difference is a summary of the response for the whole domain. Fig. 6 presents the AAV of the ΔO_3 difference between the extended mechanism and the other mechanisms for the three simulation cases.

RACM shows average differences below 5% for the three simulation domains. The reduced mechanism reaches 14% in Bogota but stays lower than 8% in Milan and Mexico City. Therefore, the three larger mechanisms show similar response to emissions reduction. On the other hand, the differences found by using the small mechanism are larger and present an important variability (19 to 40%).

5.2.2. The surface of the NO_x-sensitive area

The surface of the NO_x-sensitive regions is compared using the proportion of the domain which is determined

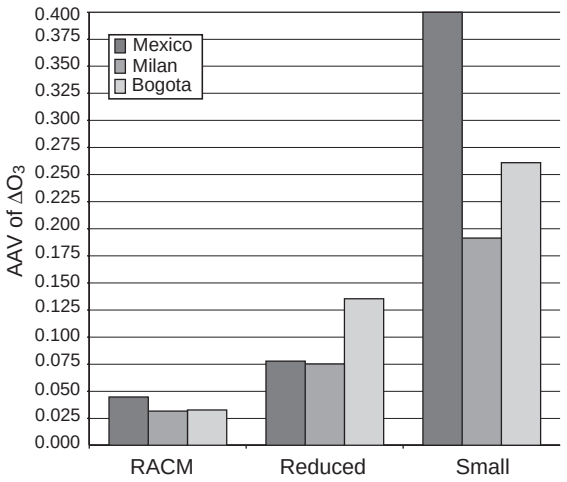

Fig. 6. Average of the absolute value of the ΔO_3 (see text for the definition) difference between the extended mechanism and the smaller mechanisms.

to be NO_x sensitive during the day. A portion of territory is considered as NO_x sensitive if ΔO_3 is positive. Table 2 presents the percentage of the domains that are NO_x sensitive for the four mechanisms.

The differences of the NO_x-sensitive areas with respect to the extended mechanism (Table 2, in brackets) are generally lower than 1.2% of the total calculation domain, except with the small mechanism on Mexico City where it is 5.7%. The small mechanism presents higher and always negative percentage differences. This denotes generally more VOC-sensitive results for this mechanism.

Table 2
Percentage of the domains that is NO_x sensitive depending on the chemical mechanism

	Extended (%)	RACM	Reduced	Small
Mexico city	54.59	54.48% (0.11)	54.57% (0.02)	60.29% (−5.70)
Milan	43.70	43.25% (0.45)	44.12% (−0.42)	44.46% (−0.76)
Bogota	69.59	69.47% (0.12)	69.43% (0.16)	70.79% (−1.20)

In brackets are presented the difference with respect to the extended mechanism.

6. CPU time comparison

The sensitivity of a chemical solver to the number of species (with respect to CPU time) depends on its numerical scheme. In a general manner, increasing the number of chemical species with an explicit and noniterative solver generates a linear increase of CPU time. An implicit or iterative solver needs a matrix inversion, which leads to a second-order growth of time consumption. The Gong and Cho's solver divides the chemical reactions in two groups (Gong and Cho, 1993): the faster reactions are solved implicitly, and the slower ones explicitly. The growth of CPU time evolves therefore neither linearly nor quadratically but somehow in between.

The simulations have been performed under SUN Solaris 8, on SUN Blade 100 workstations. All calculations simulated 29 h in the domain of Milan. The run using RACM took 5 h and 30 min to complete the simulation.

The extended mechanism is almost two times slower (1.9 times) than RACM (10 h and 30 min). With a calculation time of $2\frac{1}{2}$ h, the reduced mechanism is more than two times as fast as RACM (0.45). The small mechanism is unsurprisingly the faster ($1\frac{1}{2}$ h), with almost a fourth of the RACM CPU time (0.27).

These differences are clearly due to the number of species. To emphasise this, Fig. 7 shows the growth of the CPU time with respect to the number of species (diamonds, referring to the left-hand side axis).

The efficiency of a mechanism is a compromise between speed and accuracy. In order to find the more efficient mechanisms among the four presented in this work, the following criterion (c) has been defined:

$$c = 1 - \frac{\overline{m}}{\max(\overline{m})} \text{ with}$$

$$\overline{m} = \frac{1}{N_{\text{hour}} N_{\text{cell}}} \sum |O_{3\ \text{extended}} - O_{3\ \text{mech}}|.$$

The meaning of $\overline{m}$ is the average of the absolute value of the ozone differences between the extended and the four mechanisms tested. It represents the average error resulting from the use of a mechanism with respect to the extended mechanism. In order to have values between zero and one, $\overline{m}$ is normalised with the maximum calculated value. Then, the normalised result is inverted to reverse the axis order. By definition, c is equal to 1 for the extended (no ozone difference) and to 0 for the mechanism that presents the maximum difference. The plot of the c criterion versus the number of species shows that decreasing the number of species from 98 in the extended mechanism to 54 in the reduced mechanism has little effect on the ozone result. The larger part of the ozone difference between the small mechanism and the extended mechanism comes from the reduction to 29 species. The overall efficiency of the mechanisms can be estimated by a joint analysis of the two curves in Fig. 7. The reduced mechanism is clearly the most efficient, giving very good ozone results (c criterion close to one) with a low calculation time.

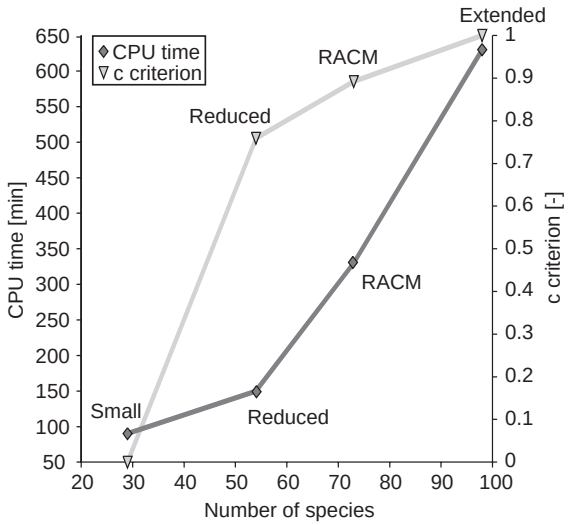

Fig. 7. The line with diamonds shows the growth of CPU time with respect to the number of species in the four tested mechanisms. One can clearly see the quadratic tendency due to the part of the equations solved with a matrix inversion. The second line is the c criterion (see the definition in the text). It emphasises the efficiency of the reduced mechanism, which give very good ozone results with a low calculation time.

7. Conclusion

When calculating a large number of emissions scenarios, smaller mechanisms can save time if they give reliable results. The goal of this work was to find an optimal parameterisation of the atmospheric chemistry that gives accurate results in a reasonable calculation time. With this intention, this study compared the response to emissions reductions of the four chemical mechanisms described in Part I (Kirchner, 2004) on three different calculation domains (Mexico City, Milan and Bogota). The cities vary by their emission concentrations and meteorological conditions. The four chemical mechanisms have been implemented in the 3D mesoscale air quality model TAPOM.

TAPOM with RACM showed its ability to simulate photochemical pollution by reproducing field measurements in the three simulation domains. The evolution of the ozone concentration is well reproduced, although the peaks may be underestimated, but not greater than 13%.

The comparison of the ozone results on the different domains show very small differences between the extended mechanism, RACM and the reduced mechanism. RACM and the reduced mechanism give similar ozone results in comparison with the extended mechanism. On the other hand, the small mechanism presents significant differences. The ozone peak is generally well reproduced with all mechanisms but is overestimated in Mexico City and Bogota with the small mechanism. The two smaller mechanisms, using the faster RO_2 parameterisation produce more RO_2 and lead to the formation of a higher amount of secondary VOC (as seen in the ALD concentration). Hence, the association of an important decrease of the number of VOC species with the faster RO_2 parameterisation as applied in the small mechanism should be used with caution, especially in highly polluted (VOC-sensitive) regions.

Two simulations with reduced emissions (35% of NO_x or VOC emissions) have been performed on the three domains. The ozone difference between the runs with VOC and NO_x reductions (noted as ΔO_3) shows the regions where VOC or NO_x reductions are more efficient in decreasing the ozone concentration. The three cities showed very different behaviour of their NO_x and VOC-sensitive regions.

The ΔO_3 differences between the extended mechanism and the three smaller mechanisms are small for RACM and the reduced mechanism but are significant for the small mechanism. The ozone reduction achieved with the NO_x or VOC emissions reduction are almost the same with RACM and the extended mechanism (differences below 5%), are overestimated by 7.5 to 14% (depending on the simulation domain) with the reduced mechanism and are overestimated by 19 to 40% with the small mechanism. The cumulated surfaces of the NO_x-sensitive areas calculated for the four chemical mechanisms do not present important differences, but the small mechanism generally presents smaller NO_x-sensitive regions.

The CPU time comparison showed that the extended mechanism is almost two times slower than RACM, more than two times slower than the reduced mechanism. The small mechanism is almost four times faster than RACM. Both RACM and the extended mechanism give similar results when the emissions are reduced. When the emission reduction scenarios are tested for ozone reduction, the addition of larger carbonyl species (as in the extended mechanism) is not recommended in mesoscale modelling, because of its higher requirements in input data and computer resources. Such parameterisations should be kept for simulations where a particularly high level of detail is needed for the chemical species. A defined c criterion evaluates, on a 0 to 1 scale, the ozone differences between the four mechanisms. The comparison of the time consumption and the c criterion for the four mechanisms highlights the reduced mechanism as being very efficient and giving reliable ozone concentration profiles in a highly acceptable time. The RO_2 parameterisation used in the reduced mechanism is therefore recommended for many photochemical pollution studies, including ozone abatement strategies or short-time ozone forecasts.

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