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USING SMOG CHAMBER DATA TO IMPROVE THE UNDERSTANDING OF SOA FORMATION

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1. INTRODUCTION

The organic fraction of secondary particles, commonly known as secondary organic aerosols (SOA), constitutes a significant part of fine aerosols. The formation of SOA is subject to complicated coupling among gas-phase chemical reactions, aqueous-phase, aerosol-phase, and meteorological processes. To correctly predict total particle concentrations in the atmosphere it is necessary to understand the physical and chemical processes producing organic aerosols. Considering that the whole complexity of the processes and factors involved in SOA formation has not been completely understood, there is a need to isolate the chemical contribution in three-dimensional photochemical models from other SOA formation origins. Measurements made under controlled environmental conditions, such as those performed in a smog chamber, offer a unique opportunity to study the chemical processes leading to SOA production. Therefore, the comparison with chamber data allows the evaluation of the chemical processes of SOA formation simulated by the chemical and aerosol modules used in CMAQ.

In order to investigate the formation processes of SOA in the smog chamber we set the box model version of CMAQ to the initial conditions of temperature, humidity, solar radiation and chemical concentrations measured at the set of experiments performed by CIEMAT during June-July 2008 in the European Photoreactor (EUPHORE) chamber, located in Valencia, Spain.

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The evolution of the concentration of each measured chemical have been modeled and compared for each experiment using four different configurations of CMAQ, testing different combinations fo the chamical models CB05 and SAPRC99 with the aerosol modules AERO4 and AERO5. The comparison of the SOA formation along with the consumption of precursors with different initial NO_x and VOC concentrations as measured in the smog chamber determines if the chemical mechanisms used in the CMAQ model can reproduce not only the maximum SOA but also their formation rate.

2. DESCRIPTION OF THE EXPERIMENTS

The aim of the experiments was to understand the SOA formation potential of a VOCs mixture oxidation in the presence of HONO under different experimental conditions. In 9 of the 10 experiments a mixture of anthropogenic VOCs was used (1,3,5-trimethylbenzene, toluene, o-xylene and octane) while in the other a biogenic mixture was selected (isoprene, α-pinene and limonene). Each experiment consisted in a variation of a specific experimental condition in comparison of the selected base case (Experiment 17). Selected conditions were the level of VOCs and HONO, the addition of different SO_2 concentrations or the role of the relative humidity.

The EUPHORE facility consists in a half-spherical teflon chamber with a volume of 300 m^3 approx., and it has been previously described by other authors (Volkamer, et al., 2001). Once the reactants have been introduced, the chamber is openend to sunlight so that the photochemical processes take place.

Initial conditions for each of the experiments are presented in Table 1.

Table 1. Initial VOCs, HONO, SO_2 (in ppb) and RH (%) conditions for the whole set of experiments. The number of the experiment makes reference to the day it was performed.

	TOL	TMB	OXYL	OCT	HONO	SO_2	RH
Exp_16	53	87	12	44	47		0.1
Exp_17	101	171	25	88	99		19.4
Exp_18	200	300	49	155	75		17.8
Exp_19	48	106	11	42	71		14.4
Exp_20	98	160	24	79	156		12.0
Exp_23	97	146	21	81	52		13.3
Exp_24	97	146	22	82	94		0.6
Exp_26	100	155	23	85	94	790	8.8
Exp_1	107	160	26	89	89	17	18.3
	APIN	**ISO**	**LIMO**				
Exp_25	105	190	104		170		11.1

3. IMPLEMENTATION OF THE CMAQ BOX MODEL

The box model implemented in this work is designed to mimic the closed system represented by the EUPHORE chamber, where transport, dispersion and deposition processes have no important relevance. Therefore, in the construction of the model, only gas phase chemical processes and aerosol formation are taken in consideration.

The chemical mechanisms CB05 and SAPRC99 coupled with the aerosol modules AERO4 and AERO5 were used in CMAQ version 4.7 in order to simulate a SOA formation experiment performed in a smog chamber. Four different combinations were used:

1. CB05 coupled with AERO4 (cb05_ae4)
2. CB05 coupled with AERO5 (cb05_ae5)
3. SAPRC99 coupled with AERO4 (saprc99_ae4)
4. SAPRC99 coupled with AERO5 (saprc99_ae5)

The system was constructed as a 4X4 equal grid cells located in Valencia, Spain (LAT: 39, LON: 0, approx.). Meteorological input files were completed with the experimental values for temperature, pressure, air density and water vapor mixing ratio.

3.1 Preprocessors compilation

Table 2 shows the lumping of each compound according to CB05 and SAPRC99 mechanisms (Carter, 2000; Yarwood, et al., 2005). Two different ICON input files were created for each experiment, one for each chemical mechanism. Aerosol modules AERO4 and AERO5 are based in the partitioning theory presented by Schell et al. (2001), and therefore a seed value for the primary aerosol is necessary in order to start the SOA formation in the model. Because of this, a value of 0.5 $\mu g/m^3$ for AORGPJ is used in each ICON input data (a higher value of 5 $\mu g/m^3$ was needed in Exp_25).

Table 2. CB05 and SAPRC99 lumping of the compounds

	CB05	SAPRC99
TOL	TOL	ARO1
1,3,5-TMB	1XYL, 1PAR	ARO2
OXYL	XYL	ARO2
OCT	7PAR, 1NR	ALK5
ISO	ISOP	ISOPRENE
APIN	TERP	TRP1
LIMO	TERP	TRP1
HONO	HONO	HONO
SO_2	SO_2	SO_2

The JPROC preprocessor was implemented using the CMAQ photolytic rates dataset for each of the days of the experiments, using in each simulation the proper chemical model.

3.2 CCTM processor

An executable file is prepared for each combination selecting the correct ModChem, ModAero and Mechanism in bldit.cctm (Table 3).

Before the executable is compiled, it is necessary to comment out in the sciproc.F file the diffusion, advection or colud processes subroutines.

Table 3. ModChem, ModAero and Mechanism selected for each simulation

Simulation	ModChem	ModAero	Mechanism
CB05_AERO4	ebi_cb05cl	aero4	cb05cl_ae4_aq
CB05_AERO5	ebi_cb05cl_ae5	aero5	cb05cl_ae5_aq
SAPRC99_AERO4	ebi_saprc99	aero4	saprc99_ae4_aq
SAPRC99_AERO5	ebi_saprc99_ae5	aero5	saprc99_ae5_aq

Once the executable file is compiled, the simulations are run according to the appropiate time run parameters.

set STTIME = 090000 - 110000 (depending on the starting time of each experiment)

set NSTEPS = 020000 - 060000 (depending on the starting time of each experiment)

set TSTEP = 000100 (1 minute time resolution for all the experiments)

4. RESULTS

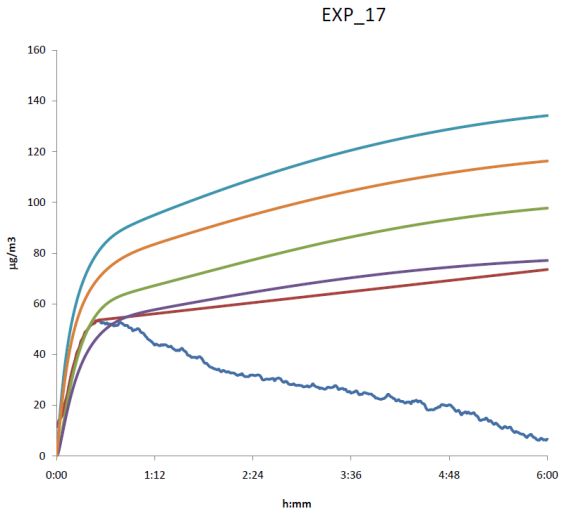

Figure 1. SOA formation in Exp_17. Original experimental data (dark blue), wall loss corrected data (red), Saprc99_ae4 (purple), CB05_ae4 (green), Saprc99_ae5 (orange) and CB05_ae5 (light blue)

When the AERO4 module was used, SOA is considered as AORGAJ, while when the AERO5 module was utilized, SOA is considered as the sum of the toluene contribution (ATOL1J, ATOL2J, ATOL3J), the xylene contribution (AXYL1J, AXYL2J, AXYL3J), the octane contribution (AALKJ) and AOLGAJ.

Figure 1 shows the general behavior observed not only in Exp_17, but also in most of anthropogenic experiments. At the beginning, the four simulations show SOA levels similar to the experimental results, but later they tend to overpredict SOA formation. When CB05 and SAPRC99 were coupled with AERO5, the overprediction was even higher. The Saprc99_ae4 (purple line) setting seems to be the most accurate combination according to the experimental data presented.

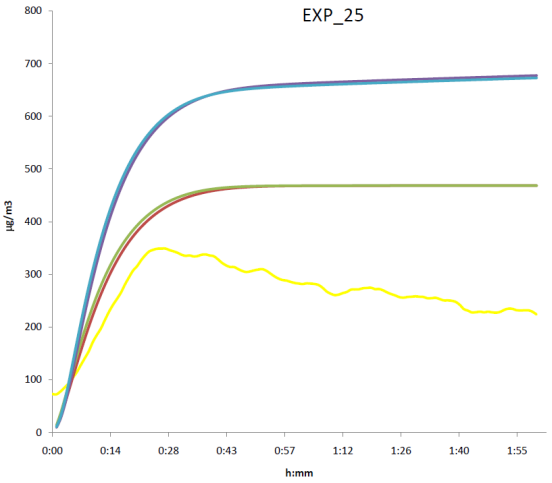

Figure 2. SOA formation in the biogenic experiment Exp_25. Original experimental data (yellow) Saprc99_ae4 (green), CB05_ae4 (red), Saprc99_ae5 (light blue) and CB05_ae5 (purple).

Figure 2 shows again an overprediction of the four simulations, but this time the two different chemical mechanisms seem to have no special relevance in SOA formation for the biogenic VOCs used, as the result with both of them when combined with AERO4 or AERO5 are almost the same.

In Exp_25, when AERO5 was used SOA was considered as the sum of the isoprene contribution (AISO1J, AISO2J, AISO3J), the terpenes contribution (ATRP1J, ATRP2J) and AOLGAJ.

Simulations for Exp_26 are presented in Figures 3 (SOA) and Figure 4 (total secondary aerosol). In this experiment a high SO_2 concentration was introduced in the chamber, so a clear contribution of the inorganic species the total secondary aerosol was expected.

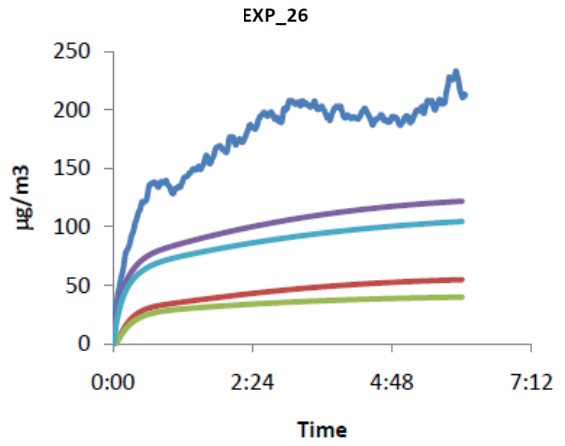

Figure 3. SOA formation in Exp_26. Original experimental data (dark blue), Saprc99_ae4 (green), CB05_ae4 (red), Saprc99_ae5 (light blue) and CB05_ae5 (purple).

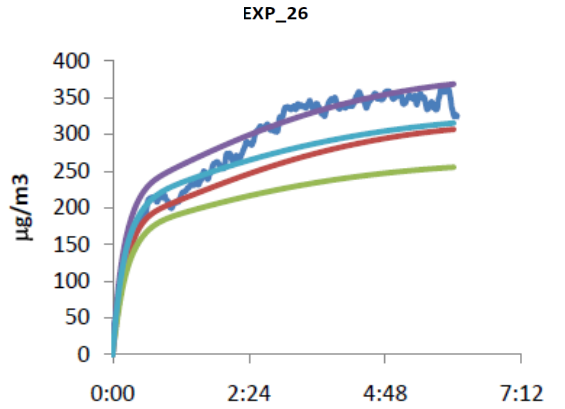

Figure 4. Total secondary aerosol formation in Exp_26. Original experimental data (dark blue), Saprc99_ae4 (green), CB05_ae4 (red), Saprc99_ae5 (light blue) and CB05_ae5 (purple).

From Figure 3, it is clear that in this experiment the simulations are underpredicting the SOA formation. However, when the inorganic species are taken in account (represented in the AERO modules as ASO4 and AH2O), the simulations predict reasonably well the total secondary aerosol formation, as it can be seen in Figure 4. This underprediction could be related to an overprediction of the inorganic species contribution to the total secondary aerosol simulated in the model and further investigation needs to be done.

5. CONCLUSION

Except for Exp_26, the four simulations tested for each experiment clearly overpredict the SOA formation. For a particular aerosol module, CB05 always predicts a higher SOA formation than SAPRC99. When AERO5 is used, a higher amount of SOA is produced and so the overprediction gets even higher. In most of the experiments tested, SAPRC99 coupled with AERO4 seems to be the most accurate combination for the simulation of the experimental data, as its overprediction is the lowest one.

Exp_26 needs further investigation in order to determine the inorganic species contribution to the aerosol formed.

6. REFERENCES

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