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EVALUATION OF DIFFERENT GAS PHASE CHEMICAL MECHANISMS AGAINST SMOG CHAMBER EXPERIMENTAL DATA

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1. INTRODUCTION

➢ Gas phase chemical mechanisms play a key role in 3-D air quality models. These mechanisms rely on kinetics and product yields of a wide variety of gas phase photo-chemical reactions carried out in smog chambers experiments. Because of the complexity of the whole atmospheric chemistry and the computational requirements of the 3-D models, these mechanisms reduce the total number of pollutants by lumping organic compounds in generic groups, according to factors such as their reactivity or their functional groups.

➢ Air quality models need a solid representation of the photo-chemical processes that occur in the real atmosphere in order to provide reliable estimations, and therefore the chemical mechanisms must be continously tested against independent experimental data sets, so that their ability to reproduce the observed evolution of the atmospheric pollutants may be evaluated

➢ In this work, we evaluate three chemical mechanisms (MELCHIOR2, CB05 and SAPRC99) by comparing model estimates against a wide data set of photo-oxidation experiments of single volatile organic compounds (VOCs) and mixtures of VOCs carried out in smog chambers.

2. SMOG CHAMBER EXPERIMENTS

Four photooxidation experiments were performed in the EUPHORE smog chamber (CEAM, Valencia, Spain)

- **20080625 and 20091029**: Biogenic VOCs + HONO
- **20091030 and 20091103**: Anthropogenic VOCs + HONO

EUPHORE CHAMBER. As the chamber opens to the sunlight, the photochemical oxidation of the VOCs starts

Initial conditions of the experiments performed in the EUPHORE chamber (Vivanco et al., 2011; Vivanco et al., 2013)

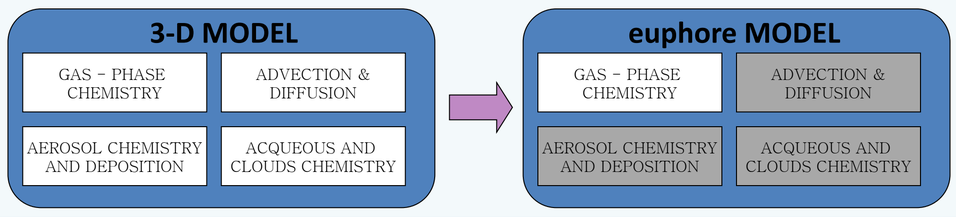
Experiment	20080625	20091029	20091030	20091103
Octane (ppb)			64	154
Toluene (ppb)			82	200
1,3,5-TMB (ppb)			118	239
o-xylene (ppb)			19	47
Isoprene (ppb)	190	99		
α-pinene (ppb)	100	59		
Limonene (ppb)	100	53		
HONO (ppb)	170	307	281	198
NO (ppb)	23	150	128	169
NO_2 (ppb)			17	24
T (K)	299-307	292-295	294-296	289-301
RH (%)	11-6	8-11	17-22	19-16

3. MODEL SET UP

Three gas-phase condensed chemical mechanisms were evaluated against The smog chamber data

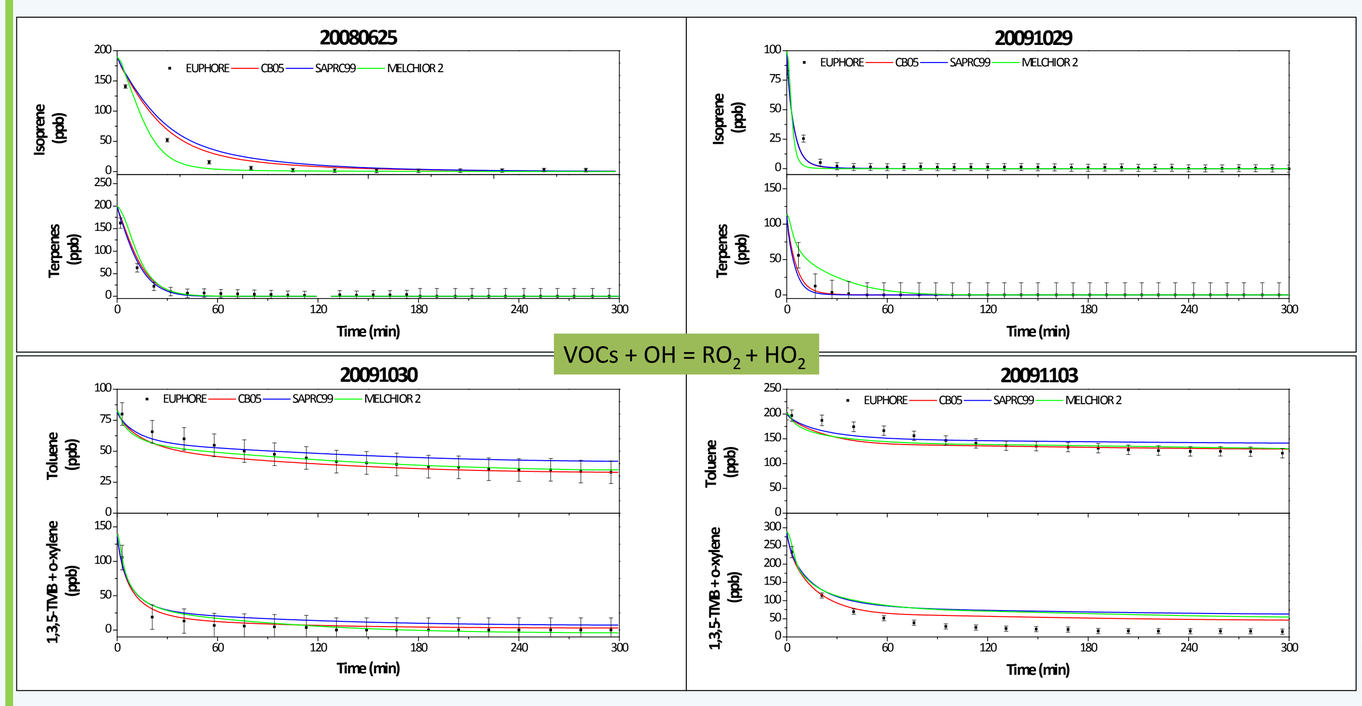
Air Quality Model	Chemical Mechanism
CHIMERE	MELCHIOR 2
CMAQ	SAPRC99, CB05

The 3-D versions of the models were simplified in order to reproduce the closed system that the EUPHORE chamber represents:



4. SIMULATION RESULTS

PARENT VOCs



VOCs + OH = RO_2 + HO_2

ISOPRENE + OH

	k (molecs cm^{-3} s^{-1})
CB05	2.54E-11*EXP(407.6/T)
SAPRC99	2.5E-11*EXP(408/T)
MELCHIOR 2	2.55E-11*EXP(410/T)

TERPENES + OH

	k (molecs cm^{-3} s^{-1})
CB05	1.5E-11*EXP(449/T)
SAPRC99	1.83E-11*EXP(449/T)
MELCHIOR 2	3.9E-11*EXP(400/T)

TOLUENE + OH

	k (molecs cm^{-3} s^{-1})
CB05	1.81E-12*EXP(355/T)
SAPRC99	1.81E-12*EXP(355/T)
MELCHIOR 2	1.81E-12*EXP(355/T)

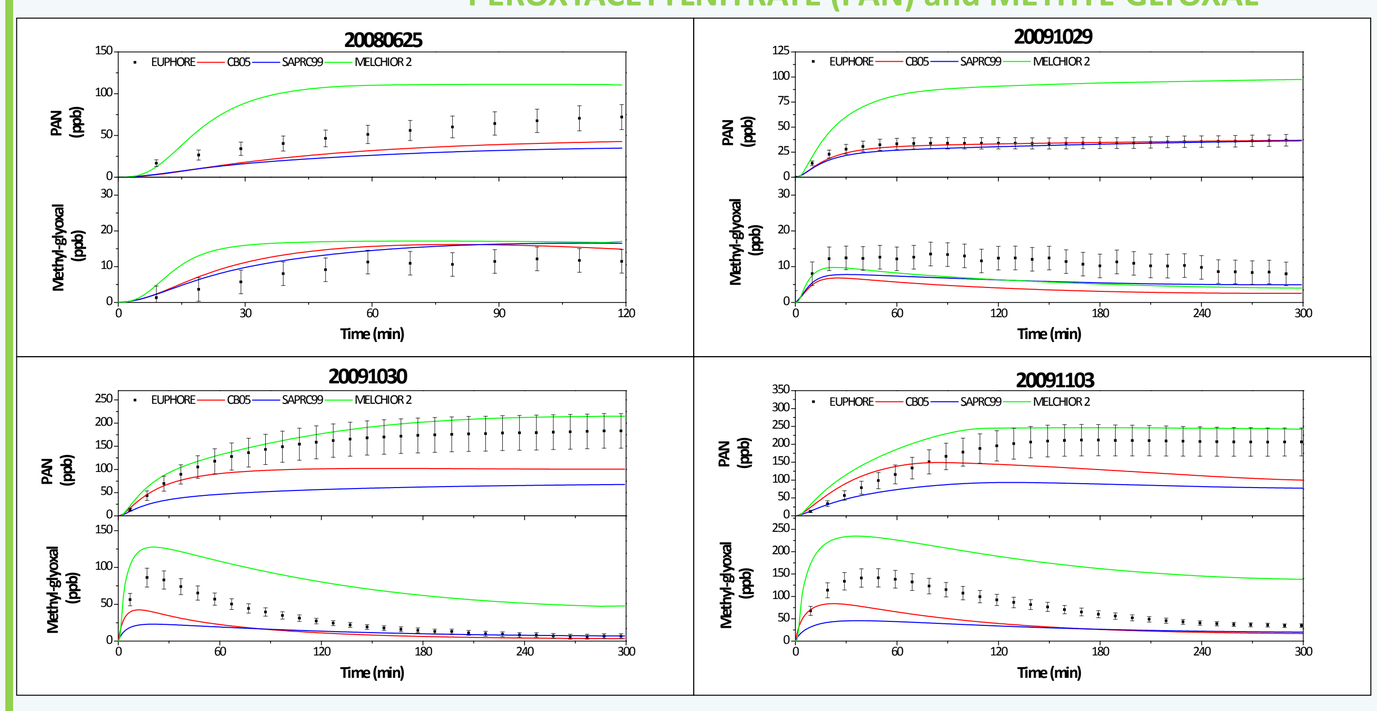
XYLENE + OH

	k (molecs cm^{-3} s^{-1})
CB05	1.7E-11*EXP(116/T)
SAPRC99	2.64E-11
MELCHIOR 2	1.37E-11

➢ The decay of the parent VOCs is produced due to their oxidation with OH radicals, generated through HONO photo-oxidation

➢ The simulation results of the three chemical mechanisms are similar due to the resemblance of their oxidation rates (*k*)

PEROXYACETYLNITRATE (PAN) and METHYL-GLYOXAL



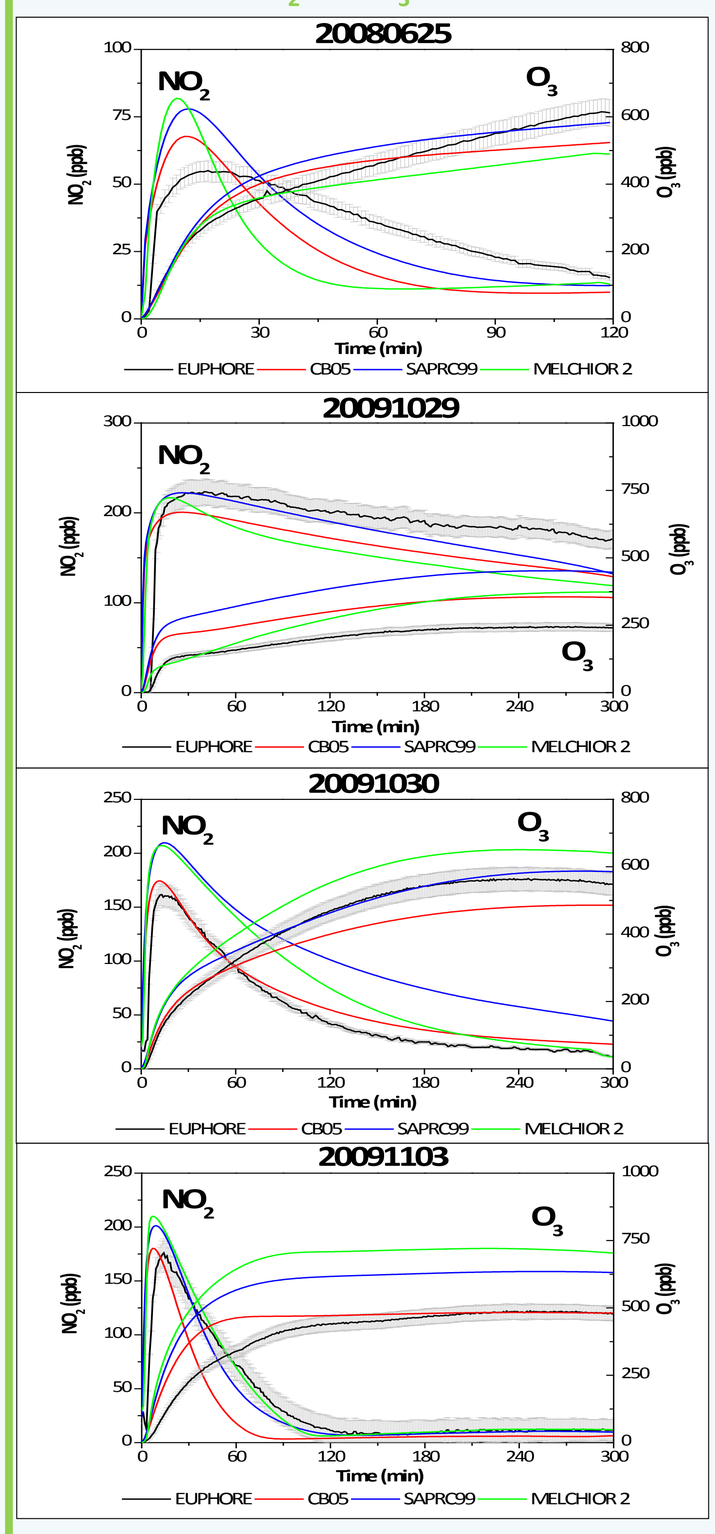
RO_2 + NO_2 <--> **PAN**
PAN + hv = RO_2 + NO_2

COV + OH -> -> **MGLYOX**
MGLYOX + OH= Prods

➢ Great differences are encountered between the experimental data and the simulations, and also amongst the mechanisms. Generally, it can be seen that MELCHIOR 2 produces higher estimations than CB05 and SAPRC99.

- PAN: its evolution is highly related to the fate of RO_2 radicals and NO_2. The formation rates of these compounds affects the subsequent PAN formation
- M-GLYOXAL: it is formed after several oxidation steps, and therefore its evolution depends on the rates of several intermediate products

NO_2 and O_3



➢ The fate of NO_2 and O_3 are highly related through the experiments. Although the mechanisms reproduce the experimental patterns, the accuracy of the simulations varies among the experiments

NO_2 peak

RO_2 + NO = RO + **NO_2**
HO_2 + NO = OH + **NO_2**

NO_2 decay and O_3 formation

RO_2 + NO_2 = PAN + …
NO_2 + hv = **O_3**

5. CONCLUSIONS

➢ The choice of a certain chemical mechanism may have a big relevance on the model simulation. The parameters employed in the condensed chemical mechanisms, based on the fitting of experiments performed in smog chambers, may be an important source of uncertainty specially on those reactions whose products distribution is not totally known

➢ As a consequence, a detailed evaluation of the chemical mechanisms employed in air quality models should be done in order to know the representation provided by the models and to enhance the simulations performed by the models

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