# MODELLING THE AEROSOL MASS FORMED IN A SMOG CHAMBER UNDER DIFFERENT VOCs/NOx CONDITIONS

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## 1. INTRODUCTION

- Secondary organic aerosols (SOA) formed from the oxidation of some anthropogenic volatile organic compounds (VOCs) are important contributors to the particulate matter levels in the lower troposphere.
- The concentration of SOA is highly dependent on the relative levels of VOCs with respect to NOx .
- The evaluation of this dependency can be carried out using air quality models and smog chamber data by creating different scenarios varying the initial VOC/NOx ratios.

## 2. EXPERIMENTS

- Experiments have been performed at the EUPHORE smog chamber (CEAM, Valencia, Spain). In these experiments, an anthropogenic VOCs mixture (toluene, o-xylene, 1,3,5-trimethylbenzene and octane) is introduced in the chamber using HONO as oxidant (Vivanco and Santiago, 2010).
- Once the chamber is opened, the sunlight enables OH production via photolysis of HONO. The OH radicals produce the photooxidation of VOCs and hence SOA formation
- Two variations are studied with respect to the base case experiment . In Case A, the VOC initial levels are increased and decreased maintaining the HONO levels approximately constant(VOCs/NOx = 12, 26 and 8). Conversely, in Case B the initial HONO levels are changed keeping the VOC approximately constant (VOCs/NOx = 12, 7 and 20)

**TABLE 1. INITIAL CONCENTRATIONS OF THE COMPOUNDS (ppbv).** BC VOCs and BC HONO make reference to the Base Case (VOCs/NOx = 12, in green) concentrations. The humidity is in the range 10-20 %. Case A and B experiments are marked in blue and orange respectively.

| TOLUENE | 1,3,5-TMB | o-XYLENE | OCTANE | HONO | VOCs/NOx | VARIATION WITH RESPECT TO THE BASE CASE |
|---|---|---|---|---|---|---|
| 101 | 171 | 25 | 88 | 99 | **12** | |
| 200 | 300 | 49 | 155 | 75 | **26** | 2*[BC VOCs] |
| 48 | 106 | 11 | 42 | 71 | **8** | 0.5*[BC VOCs] |
| 98 | 160 | 24 | 79 | 156 | **7** | 1.5* [BC HONO] |
| 97 | 146 | 21 | 81 | 52 | **20** | 0.5* [BC HONO] |

## 3. CMAQ SIMULATIONS

- Two CMAQ 4.7 simulations have been performed for each experiment, combining the two gas phase mechanisms available in the model (CB05 and SAPRC99) with the latest aerosol module (AERO5) (Carlton et al., 2010).
- Gas phase mechanisms have been modified in order to consider some important wall chamber reactions previously characterized for the EUPHORE chamber (Bloss et al., 2005).
- Apart from the semivolatile SOA species, AERO5 also considers nonvolatile SOA species which do not partition back to the gas phase. Among these species are the low-NOx aromatic SOA (AXYL3J, ATOL3J) and oligomers formed through particle phase reactions (AOLGAJ)

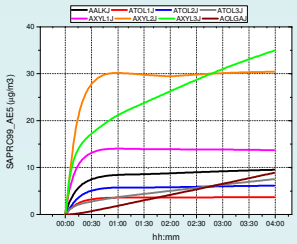


**FIGURE 1. AERO5 SOA SPECIES FOR THE BASE CASE EXPERIMENT.** Nonvolatile species (ATOL3J, AXYL3J and AOLGAJ) are continuously growing because they do not partition back to the gas phase

- Aromatic SOA is treated as the sum of the products of two competitive reactions involving the peroxy radical RO2. The relative importance of each reaction depends on the NOx level in the system.

TOL, TMB, OXYL + OH → RO2

- NO → ATOL1J, ATOL2J, AXYL1J, AXYL2J (High-NOx pathway SOA)
- HO2 → ATOL3J, AXYL3J (Low-NOx pathway SOA)

## 4. RESULTS

### SOA/NOx/VOCs SYSTEM

- SOA concentration is measured in the chamber using a tapered element oscillating monitor (TEOM). The capacity of each experiment to produce SOA will be used to implement an experimental SOA/NOx/VOCs system to understand the effects of different VOCs/NOx ratios.

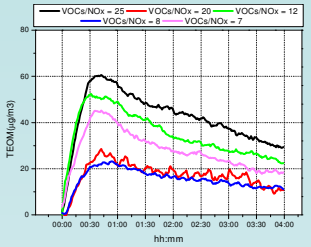


**FIGURE 2. RAW SOA TEOM TIMESERIES.** SOA values measured 1 hour after the opening of the chamber (00:00) are used to suggest an experimental SOA/NOx/VOCs system

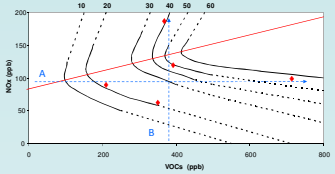


**FIGURE 3. EXPERIMENTAL SOA/NOx/VOCs SYSTEM.** Based on the SOA measured in the chamber, two different NOx-VOCs regimes are separated by the red line (Vivanco et al., 2011)

### SIMULATION RESULTS

- Experimentally measured SOA concentration profiles are compared with the results of the simulations. SOA concentration was corrected for dilution and wall losses ($k_{total\_loss}$ = 5 – 8E-5 s-1)

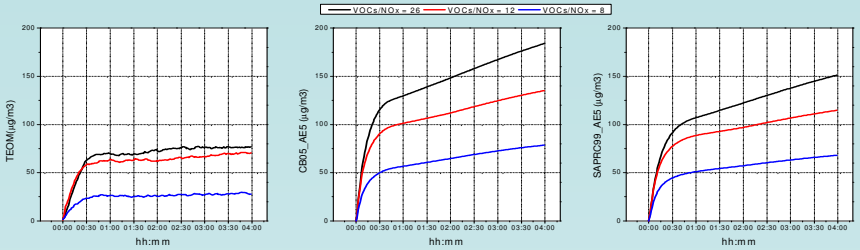


**FIGURE 4. SOA SIMULATION RESULTS FOR THE VOCs LEVEL CHANGING EXPERIMENTS (CASE A).** Both SAPRC99 and CB05 overpredict the mass of SOA formed in the three experiments. However, the response of the simulations to the increase and decrease of the initial VOCs concentration is similar to that observed in the experimental data from the chamber.

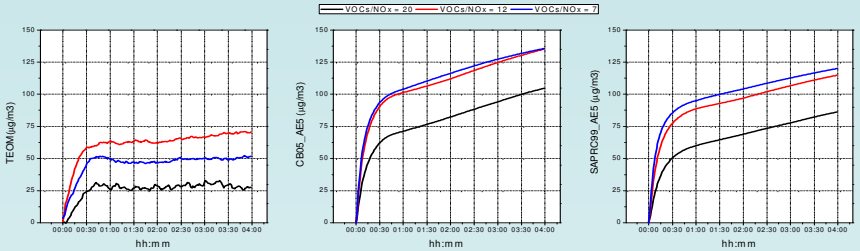


**FIGURE 5. SOA SIMULATION RESULTS FOR THE NOx LEVEL CHANGING EXPERIMENTS (CASE B).** Overpredictions are also found in this scenario. In addition, the response of the simulations to the variations in HONO initial concentrations differ from the experimental data. The change in the NOx-VOCs regime observed in the experimental data (Figure 2) is not observed in the model simulations.

## 5. CONCLUSIONS

- All the simulations tested show an overprediction of the SOA mass formed in the chamber. This overprediction seems to be related to the aerosol module, since it occurs independently of the two gas phase mechanisms are used.
- The performance of the simulations in Case A shows that an increase of SOA is observed when the initial VOCs concentration is increased, for a fixed HONO concentration. This is in agreement with the experimental data, regardless of the observed overprediction.
- The results of the simulations in Case B show an enhancement of SOA formation when the initial HONO concentration is increased. However, the experimental data show a two regime behaviour, as presented in Figure 2. In the first regime SOA increases with HONO (VOCs/NOx = 20 to 12) and in the second regime SOA formation is inversely related with the initial HONO concentration (VOCs/NOx = 12 to 7). The boundary between these two regimes is observed at a VOCs/NOx ratio between 12 and 7.

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## 6. REFERENCES

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## 7. ACKNOWLEDGEMENTS

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