# SO2 effect on Secondary Organic Aerosol Formation: Experimental And Modelled Results

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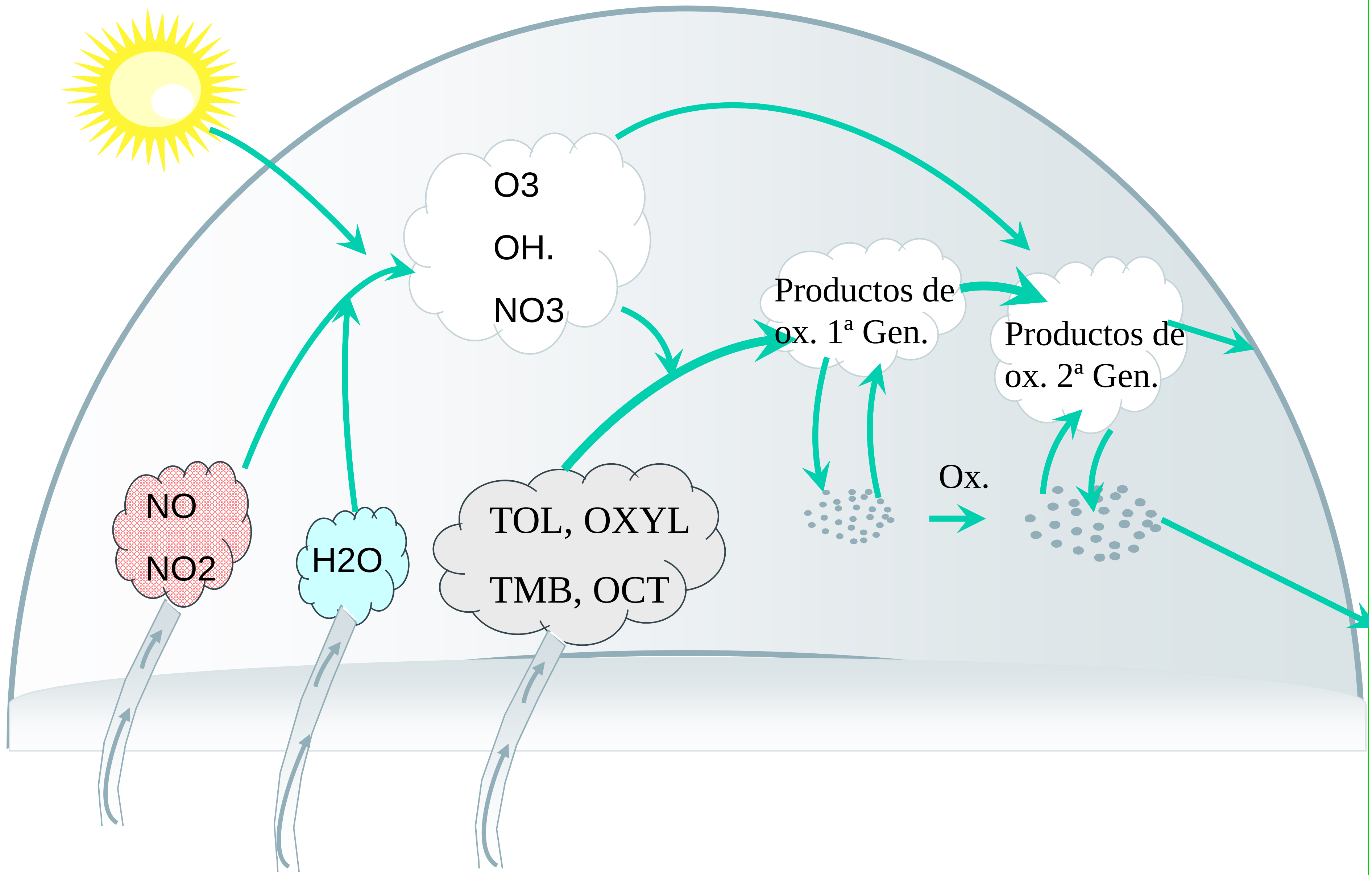
**14th HARMO**

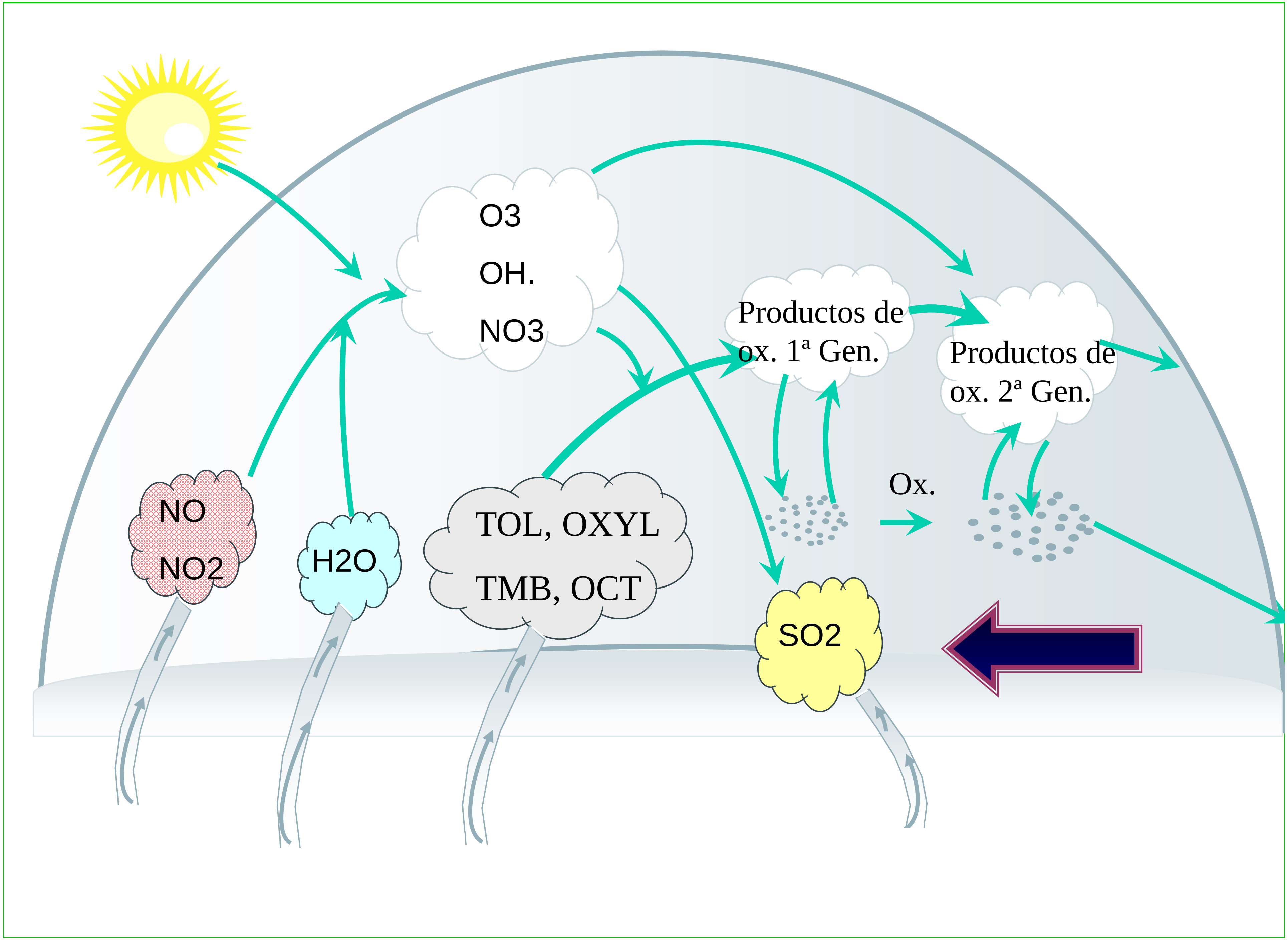
*Kos Island, Greece, 2-6 October 2011*

# This presentation will be focused on:

- The analysis of the capability of **TWO AIR QUALITY MODELS** (***CMAQ, CHIMERE***, *reduced versions*) to simulate the formation of SOA under acidic conditions, considering some experimental data (***EUPHORE chamber, CEAM, Valencia, Spain***).

# EUPHORE CHAMBERS. CEAM, Valencia, SPAIN


O3
OH.
NO3
Productos de
ox. 1ª Gen.
Productos de
ox. 2ª Gen.
Ox.
NO
NO2
H2O
TOL, OXYL
TMB, OCT


O3
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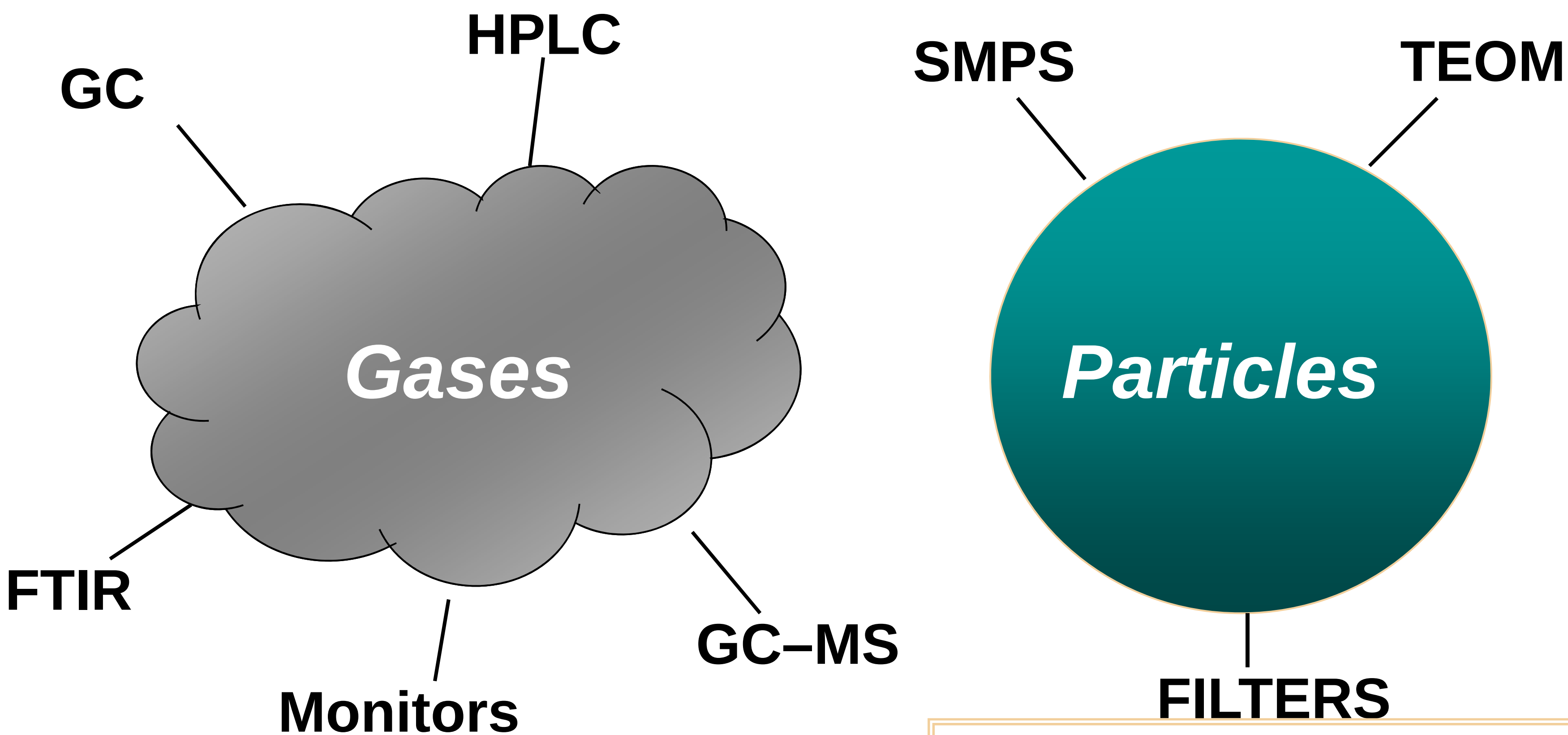
SO2




**($O_3$, HCHO, $NO_2$, CO, $SO_2$)**

**Humidity, Temperature, Pressure**

1. **IONIC CROMATOGRAPHY (sulphates and nitrates)**
2. **GC-MS Varian Organic characterization**

***Gas chromatography coupled to a mass spectrometer (GC-MS) infrared instrumentation (FTIR); Scanning mobility particle sizer (SMPS); Tapered element oscillating monitor (TEOM); High performance liquid chromatography (HPLC)***

Initial conditions. **Concentration in ppb**. **RH in %.** *Submitted to Atmos. Envir. as short commun., Vivanco et al. 2011)*

**ANTHROPOGENIC EXPERIMENTS**

| | TMB | TOL | OXYL | OCT | HONO | NO | $NO_2$ | $SO_2$ | RH |
|---|---|---|---|---|---|---|---|---|---|
| **20090610**** | 131 ± 15 | 87 ± 14 | 22 ± 4 | 87 ± 18 | 122 ± 5 | 59 ± 2 | | | 17-4 |
| **20090622**** | 19 ± 5 | 116 ± 18 | 29 ± 4 | 10 ± 2 | 119 ± 6 | 57 ± 5 | | | 14-17 |
| **20090623**** | 101 ± 28 | 81 ± 13 | 22 ± 3 | 75 ± 15 | | 34 ± 3 | 69 ± 5 | | 17-18 |
| **20091006*** | 129 ± 13 | 86 ± 23 | 24 ± 11 | 73 ± 38 | 90 ± 3 | 31 ± 2 | | | 37-28 |
| **20091007**** | 122 ± 23 | 82 ± 16 | 19 ± 4 | 71 ± 14 | 79 ± 5 | 118 ± 8 | 57 ± 4 | | 46-52 |
| **20091008*** | 121 ± 36 | 84 ± 25 | 23 ± 12 | 72 ± 35 | 292 ± 19 | 261 ± 17 | 80 ± 5 | | 0.5-1 |
| **20091030*** | 118 ± 10 | 82 ± 9 | 19 ± 11 | 64 ± 38 | 281 ± 18 | 128 ± 8 | 17 ± 1 | | 17-22 |
| **20091103*** | 239 ± 20 | 200 ± 12 | 47 ± 14 | 154 ± 38 | 198 ± 12 | 169 ± 10 | 24 ± 1 | | 19-16 |

**BIOGENIC EXPERIMENTS**

| | ISO | APIN | LIMO | | HONO | NO | $NO_2$ | $SO_2$ | RH |
|---|---|---|---|---|---|---|---|---|---|
| **20090624***** | 107 ± 3 | 66 ± 5 | 58 ± 4 | | 99 ± 6 | 34 ± 2 | 128 ± 1 | | 0.5-3 |
| **20091005**** | 121 ± 34 | 64 ± 18 | 56 ± 16 | | | 43 ± 3 | 26 ± 2 | | 17-11 |
| **20091014***** | 92 ± 3 | 50 ± 5 | 50 ± 4 | | 87 ± 5 | 48 ± 3 | | | 30-26 |
| **20091026*** | 122 ± 33 | 71 ± 18 | 40 ± 10 | | 53 ± 3 | 41 ± 2 | | | 19-22 |
| **20091027**** | | 63 ± 18 | 65 ± 18 | | 101 ± 7 | 32 ± 2 | | | 8-13 |
| **20091029*** | 99 ± 28 | 59 ± 12 | 53 ± 13 | | 307 ± 20 | 150 ± 10 | | | 8-11 |

**MIXED EXPERIMENT**

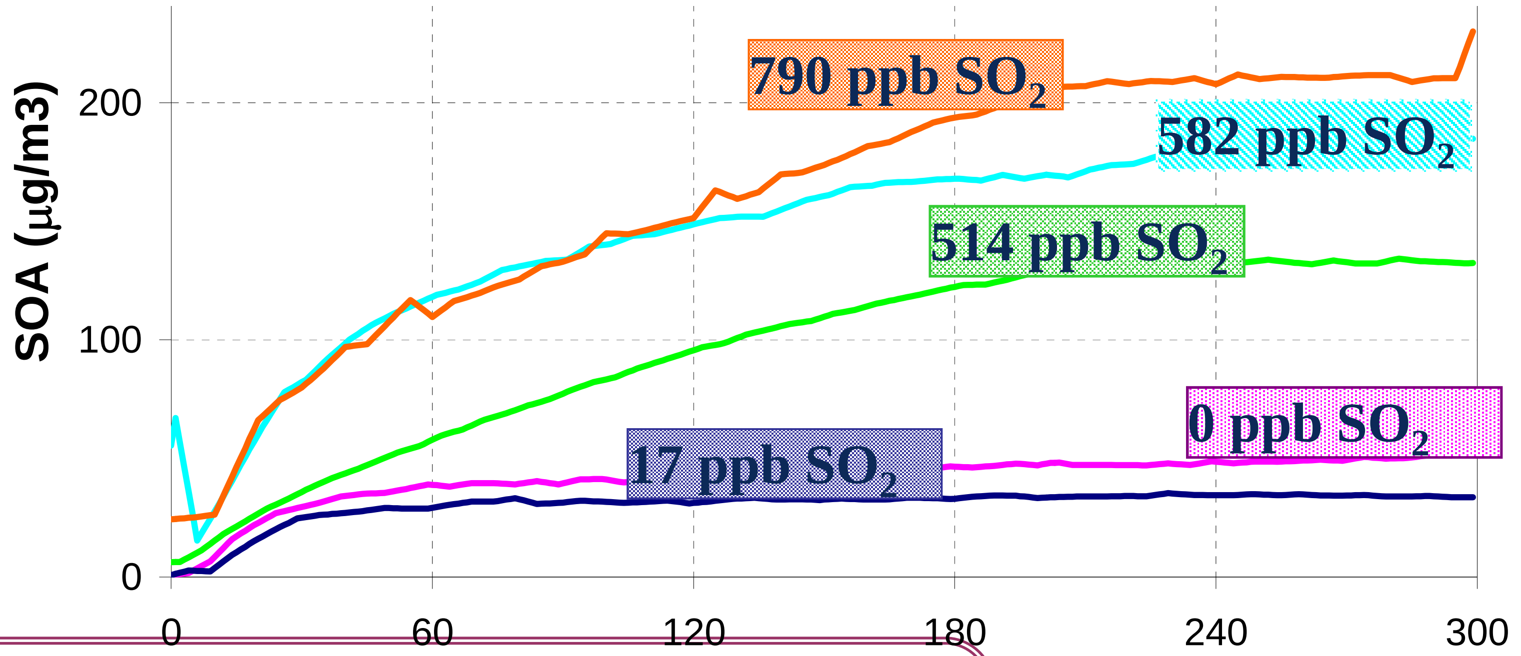
| | TMB | TOL | OXYL | OCT | HONO | NO | $NO_2$ | $SO_2$ | RH |
|---|---|---|---|---|---|---|---|---|---|
| **20091106*,***** | 30.2 ± 7 | 166.8 ± 20 | 39 ± 11 | 24.6 ± 7 | 104.8 ± 7 | 141 ± 9 | 58.8 ± 4 | | 0.4-3 |
| | **BENZ** | **ISO** | **APIN** | **LIMO** | | | | | |
| | 39.1 ± 11 | 16.6 ± 3 | 16.6 ± 5 | 11.8 ± 4 | | | | | |

** GC, ** GCMS, *** FTIR; HONO is measured with FTIR; NO, $NO_2$ and $SO_2$ are measured with monitors.*

| | TMB ppb | TOL ppb | OXYL ppb | OCT ppb | HONO ppb | NO ppb | $NO_2$ ppb | $SO_2$ ppb | RH % | T K |
|---|---|---|---|---|---|---|---|---|---|---|
| **A1** | 171 | 101 | 25 | 88 | 99 | 19 | | | 19-10 | 296-305 |
| **A2** | 160 | 107 | 26 | 89 | 89 | | | **17** | 18-9 | 298-307 |
| **A3** | 116 | 84 | 18 | 72 | 57 | 182 | 128 | **514** | 47-62 | 299-297 |
| **A4** | 204 | 106 | 23 | 87 | 89 | 126 | 36 | **582** | 16-25 | 302-307 |
| **A5** | 155 | 100 | 24 | 85 | 94 | 15 | | **790** | 9-4 | 299-307 |

| Day | TOL | TMB | OXYL | OCT | HONO | $SO_2$ | RH |
|---|---|---|---|---|---|---|---|
| | μg/m³ | μg/m³ | μg/m³ | μg/m³ | μg/m³ | μg/m³ | % |
| 6/16/08 | 205 | 440 | 54 | 211 | 923 | | 0.1 |
| 6/18/08 | 767 | 1501 | 217 | 737 | 147 | | 17.8 |
| 6/19/08 | 184 | 530 | 49 | 200 | 139 | | 14.4 |
| 6/20/08 | 378 | 804 | 107 | 377 | 307 | | 12.0 |
| 6/23/08 | 371 | 729 | 93 | 384 | 102 | | 13.3 |
| 6/24/08 | 371 | 728 | 97 | 388 | 183 | | 0.6 |
| | **APIN** | **ISO** | **LIMO** | | | | |
| | μg/m³ | μg/m³ | μg/m³ | | | | |
| 6/25/08 | 591 | 535 | 585 | | 330 | | 11.1 |

# *Experimental results*




**Higher SOA production for high initial SO2**

- The inorganic content of the aerosol was determined by analitycal methods described in a previous paper [Vivanco et al., 2011b].
- Inorganic characterization (%) of the filtered aerosol mass collected in the experiments:

| | **(A1)** | **(A2)** | **(A3)** | **(A4)** | **(A5)** |
|---|---|---|---|---|---|
| **Nitrates (%)** | 4-8.5 | 2.5-5 | *1.7-2.1** | 1.7-2.1 | 1-2.5 |
| **Sulphates (%)** | 1-2.0 | 4-10.5 | *28-31** | 28-31 | 33-44 |

** As no filter was available, values for A4 were used.*

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## RESULTS

$$Y = \frac{\Delta Mo}{\Delta ROG}$$

| Exp. | $VOC_o$ (μg/m³)[a] | $HONO_o$ (μg/m³) | $\Delta ROG$ (μg/m³)[a] | $\Delta Mo$ (μg/m³) | $Y_{SOA}$ (%) |
|---|---|---|---|---|---|
| 6/16/08 | 913.81 | 92.25 | 762.31 | 18.78 | 2.5 ± 0.3 |
| 6/17/08 | 1776.03 | 193.09 | 1025.64 | 52.36 | 5.1 ± 1.5 |
| 6/18/08 | 3208.96 | 147.05 | 1359.54 | 60.66 | 4.5 ± 2 |
| 6/19/08 | 960.13 | 139.76 | 733.26 | 23.22 | 3.2 ± 0.3 |
| 6/20/08 | 1661.52 | 305.85 | 1211.34 | 43.65 | 3.6 ± 0.5 |
| 6/23/08 | 1575.92 | 101.01 | 531.76 | 28.64 | 5.4 ± 3.7 |
| 6/24/08 | 1578.63 | 182.91 | 924.30 | 53.49 | 5.8 ± 1.8 |
| 6/25/08 | 1665.69 | 332.88 | 1710.59 | 348.94 | 20.4 ± 5.2 |
| 6/26/08 | 1739.12 | 171.23 | 1589.15 | 235.52 | 14.8 ± 1.8 |
| 7/01/08 | 913.81 | 173.23 | 1061.70 | 31.31 | 3 ± 0.6 |

## ANTRHOPOGENIC PRECURSORS

| Exp | Y_SOA (%) |
|---|---|
| 180608 | 4.5 |
| 230608 | 4 |
| 170608 | 5.1 |
| 190608 | 3.2 |
| 200608 | 3.6 |
| 31109 | 4.3 |
| 301009 | 7.5 |
| 240608 | 5.8 |
| 220609 | 7.8 |
| 260608 | 14.8 |
| 70108 | 3 |

## BIOGENIC PRECURSORS

| Exp | Y_SOA (%) |
|---|---|
| 51009 | 14.1 |
| 261009 | 18.6 |
| 250608 | 20.40 |
| 141009 | 18.9 |
| 271009 | 29.6 |
| 240609 | 21.6 |
| 70619 | 25.7 |
| 291009 | 23.2 |

EXP WITHOUT ISOPRENE

(JUST APIN + LIM)

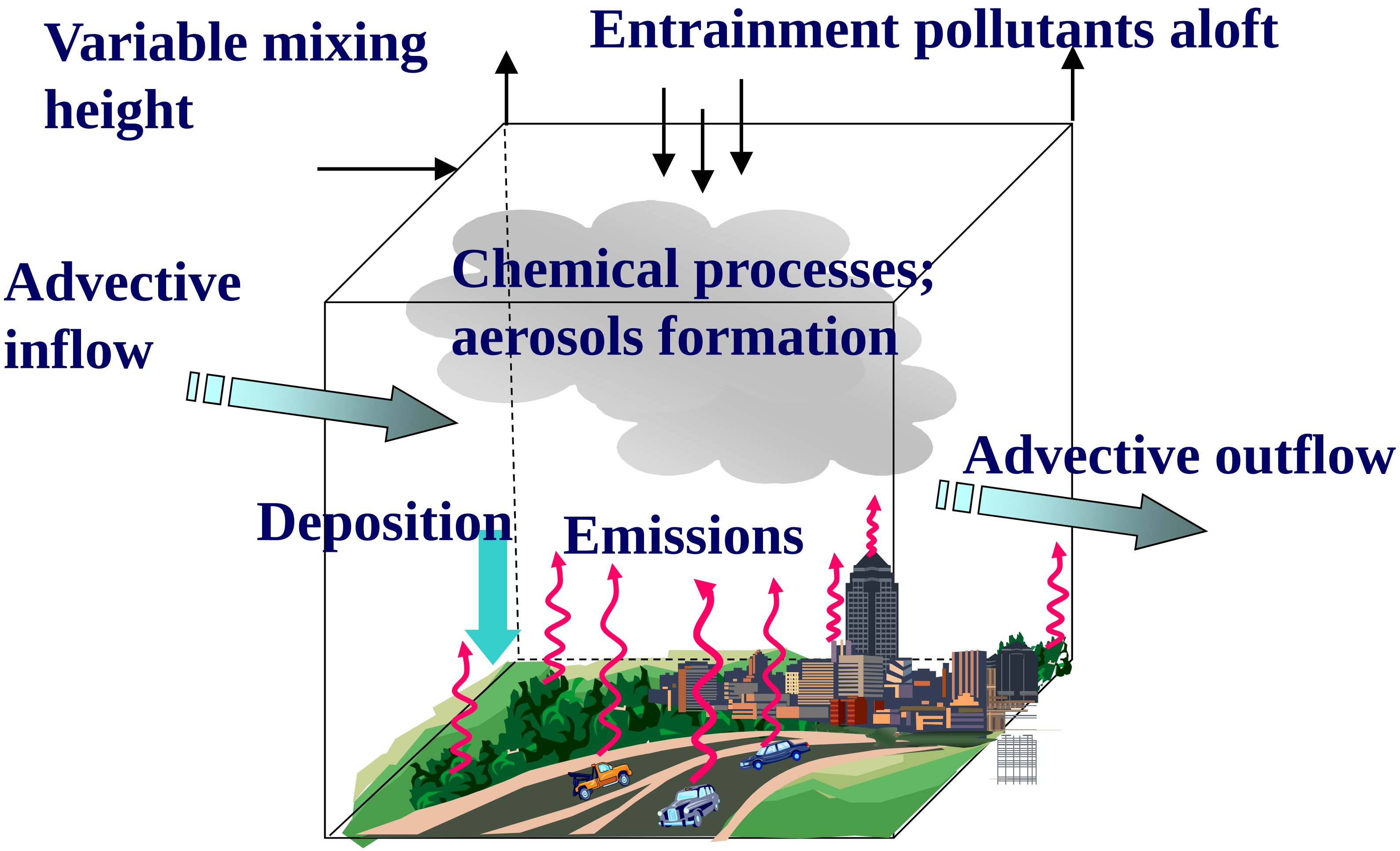
# *Experimental results…*

# *Model setup…*

# Model set-up

- 1st. Prepare a ***reduced version*** of ***CHIMERE*** and ***CMAQ***

We changed the code of these models, as they are 3D models (by discounting advection, turbulence, deposition, emissions).



Variable mixing height
Entrainment pollutants aloft
Advective inflow
Chemical processes; aerosols formation
Advective outflow
Deposition
Emissions

$$\frac{\partial \overline{C_i}}{\partial t} = -\nabla \cdot (\bar{u}\,\overline{C_i}) + \nabla \cdot (k\,\nabla \overline{C_i}) + \quad + Q_i + D_i + $$

Advection

Turbulence

Chemical reactions

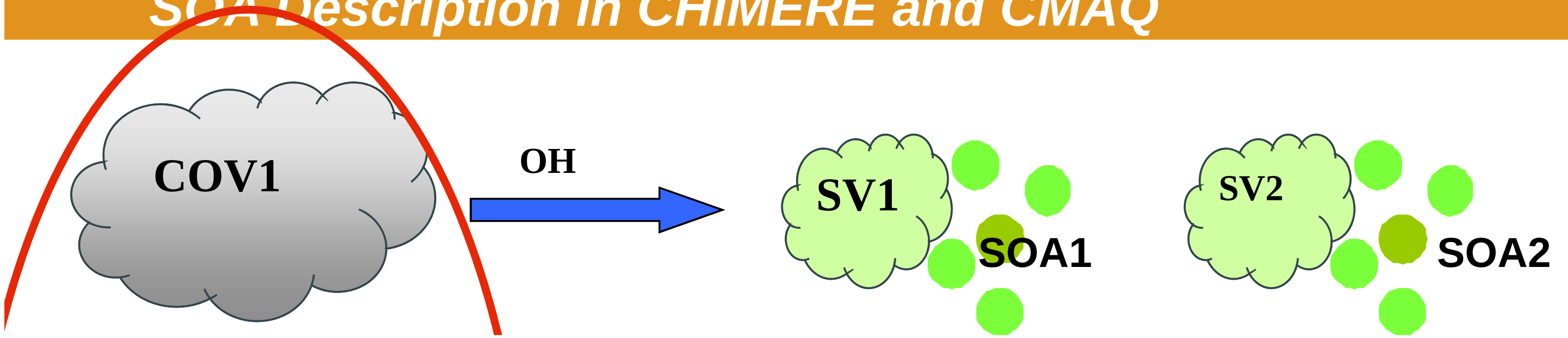
Emissions

Deposition

Aerosol processes (nucleation, coagulation, SOA,..)

***Brief description of SOA mechanism in CHIMERE and CMAQ…***

***(for anthropogenic precursors)***


COV1
OH
SV1
SOA1
SV2
SOA2

## SOA Description in CHIMERE

| Lumped precursors | Hydrophilic SOA | Hydrophobic SOA |
|---|---|---|
| Monosubstituted aromatics (toluene and others) and benzene | AnA0D, AnA1D, AnA2D | AnBmP, AnBlP |
| Polysubstituted aromatics (xylenes and trimethylbenzenes) | **AnA0D, AnA1D,AnA2D** | **AnBmP, AnBlP** |
| **Long alkanes** | | **AnBmP** |

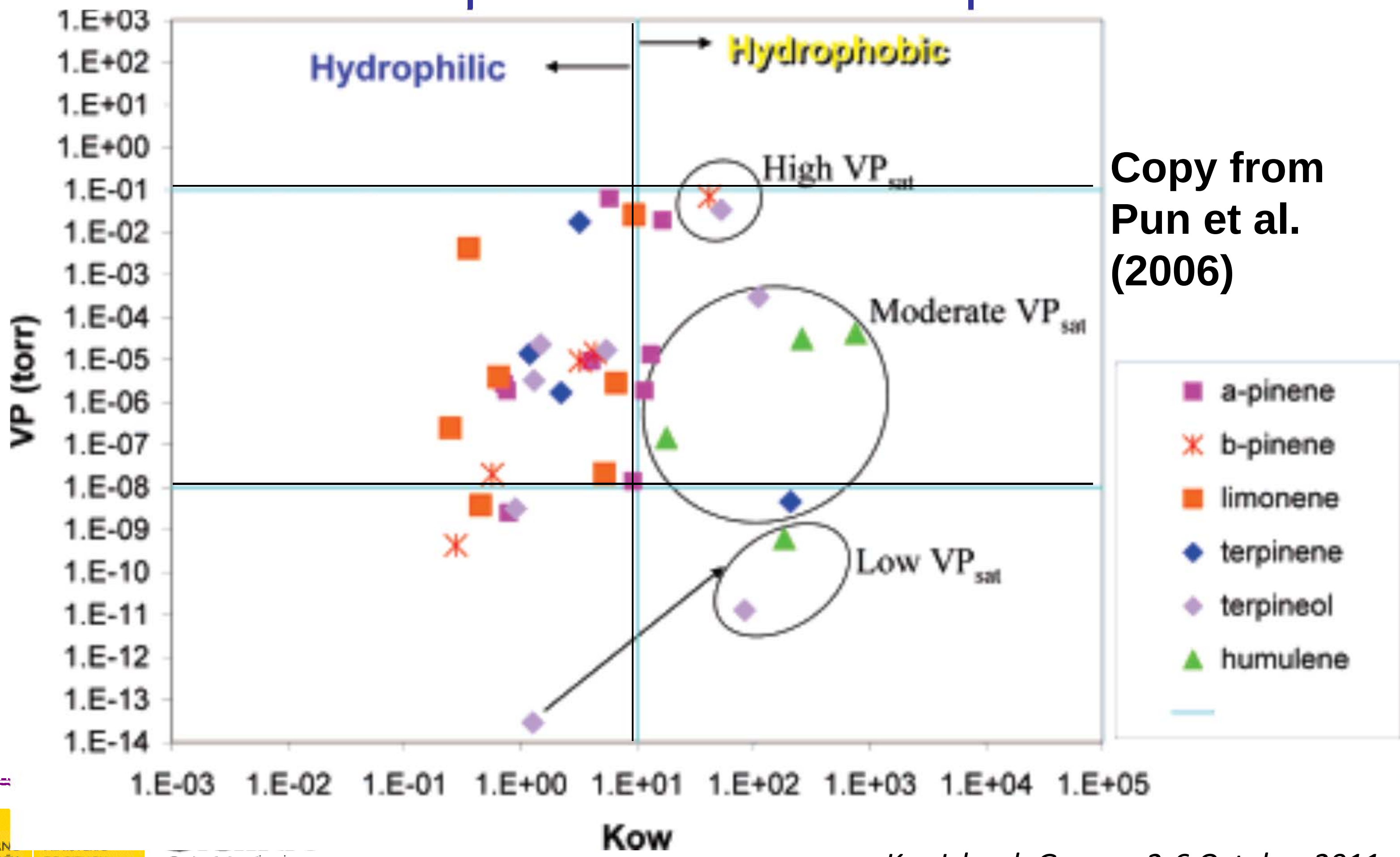
## SOA Description in CMAQ

| Lumped precursors | Semivolatile SOA | Nonvolatile SOA |
|---|---|---|
| Long alkanes | AALK | |
| Benzene | ABZN1, ABZN2, | ABZN3 |
| High yield aromatics (toluene) | ATOL1, ATOL2 | ATOL3 |
| Low yield aromatics (xylenes and trimethylbenzenes) | AXYL1, AXYL2 | AXYL3 |

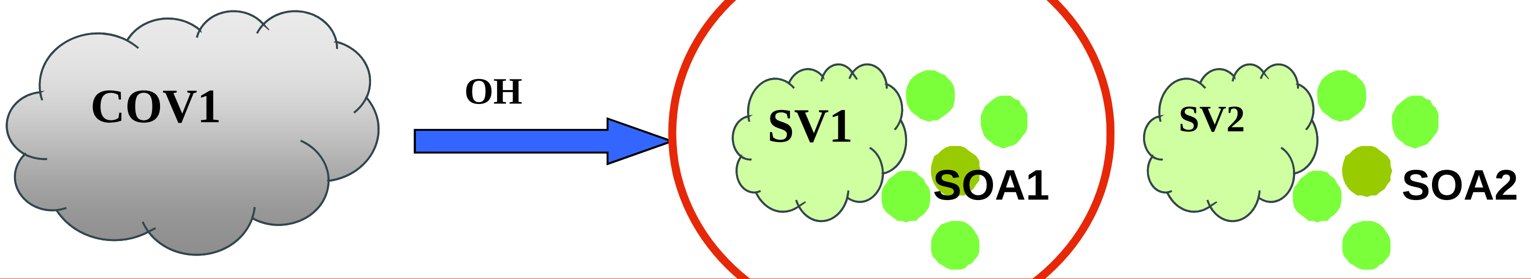
***Hydrophilic: most likely to dissolve into aqueous inorganic particles***
***Hydrophobic SOA that are most likely to absorb into organic particles***

*K*ow value of 10 was used as the criterion separating hydrophilic (*K*ow < 10) and hydrophobic (*K*ow>10) compounds.

**octanol/water coefficient (Kow)**




**Copy from Pun et al. (2006)**




Raoult's law (in CHIMERE hydrophobic species):

$$K_i = \frac{RT}{10^6 MW_{OM} \gamma_i P_i^{sat}}$$

*R : ideal gas law constant ($m^3$ atm/mol/K)*

*T : temperature (K)*

*$MW_{OM}$ : mean molecular mass of the organic particulate phase*

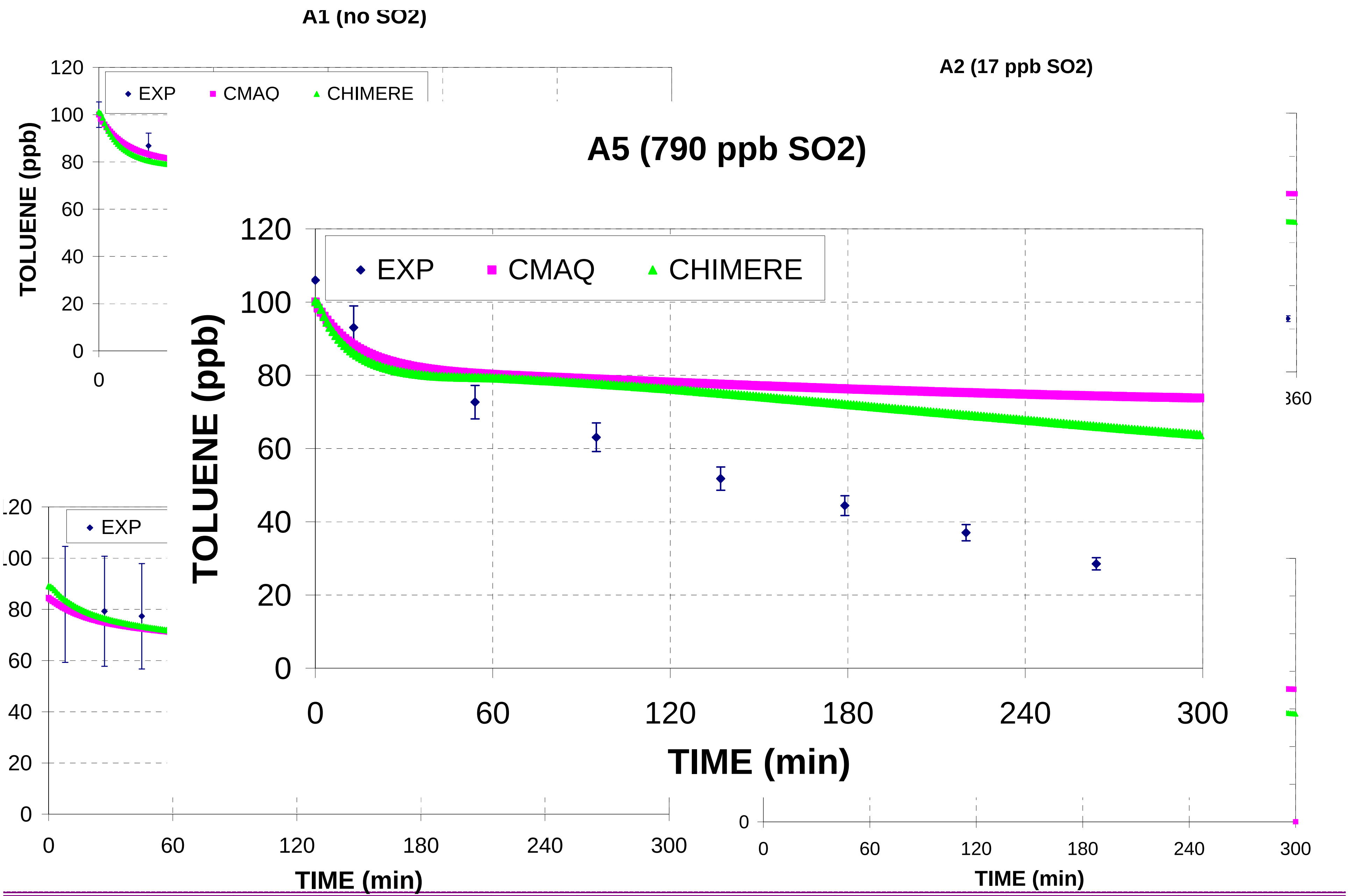
*$\gamma_i$ : activity coefficient*

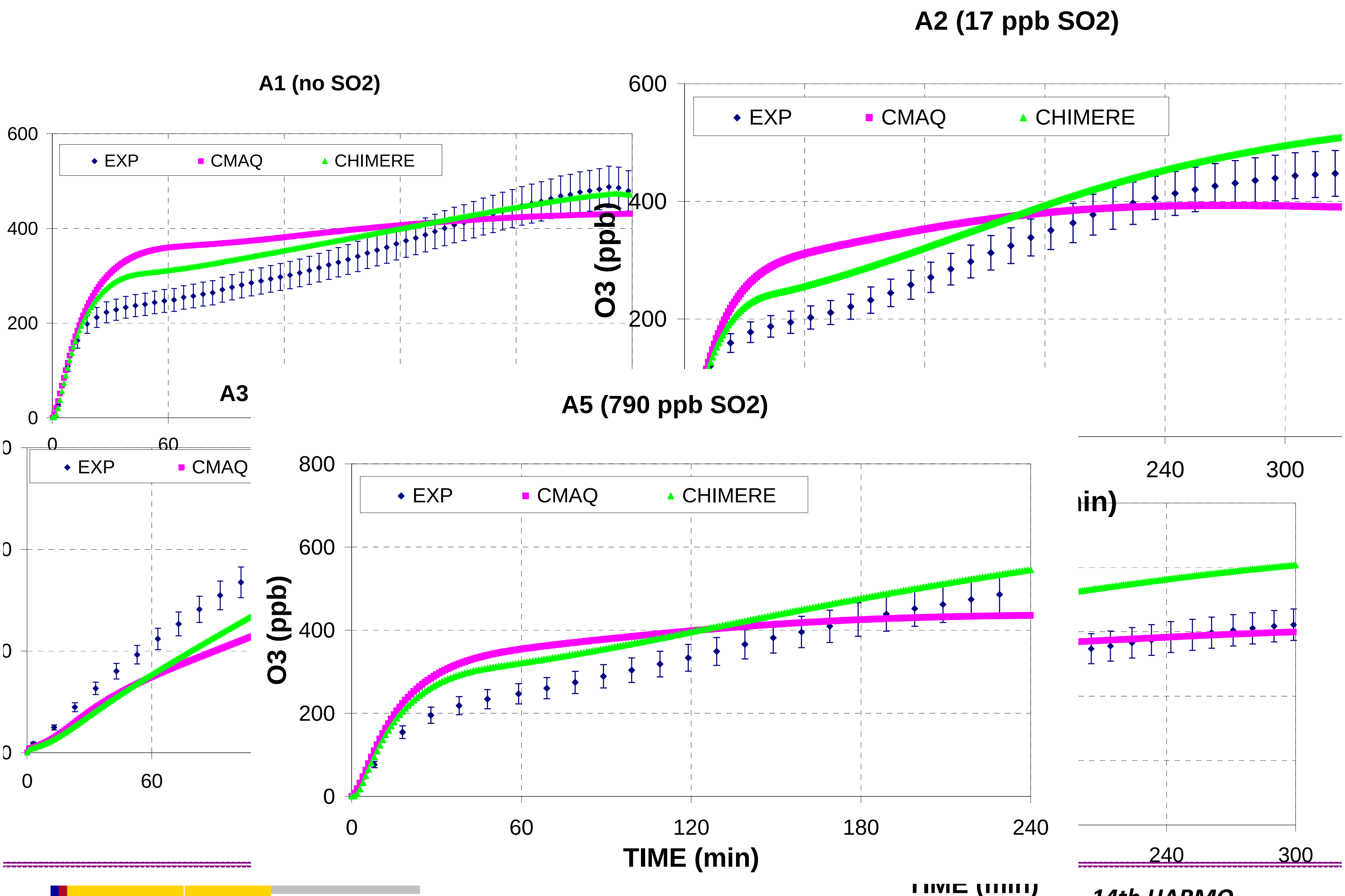
*$P_i^{sat}$ : saturation vapor pressure (atm)*

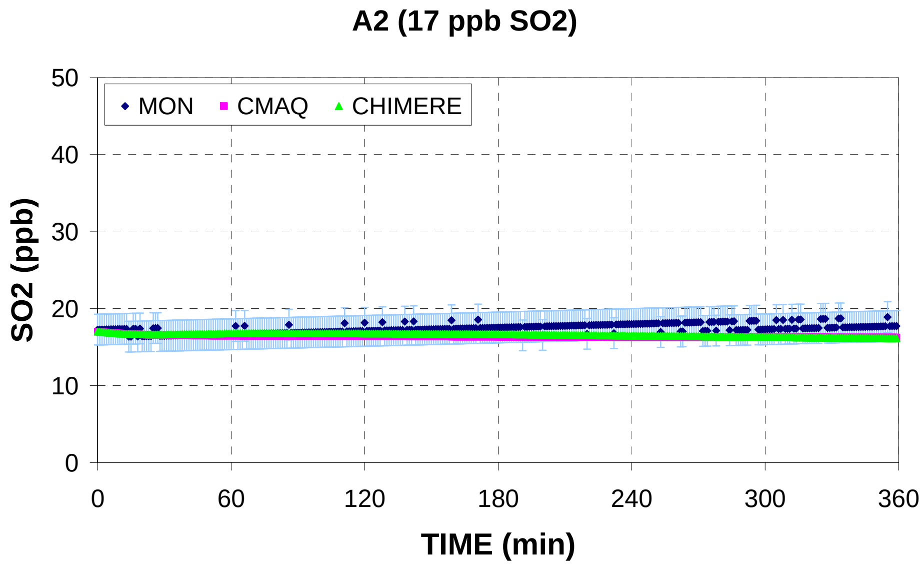
Equilibrium partitioning coefficients

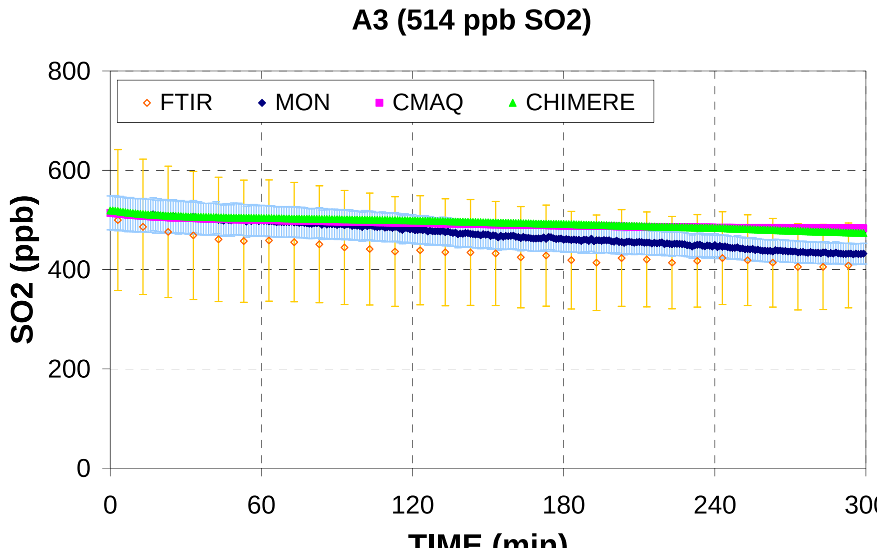
# *Some modelling results…*

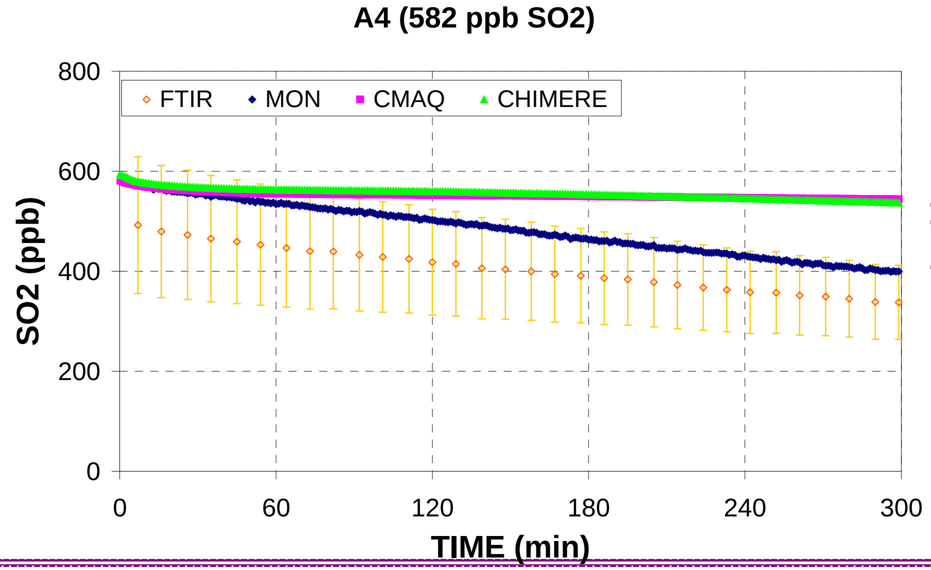
## *Gas phase*

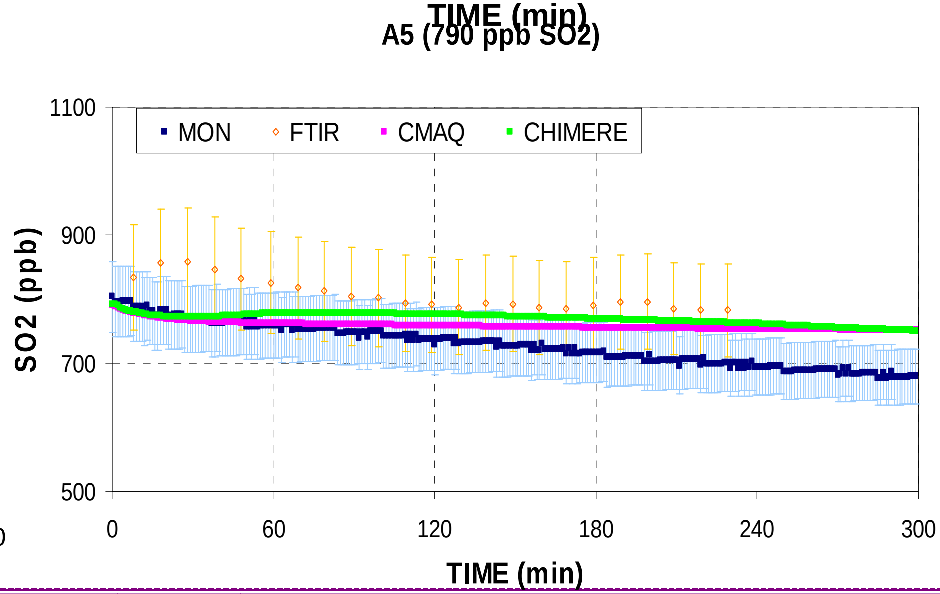

A1 (no SO2)
A2 (17 ppb SO2)
A5 (790 ppb SO2)
EXP
CMAQ
CHIMERE
TOLUENE (ppb)
0
20
40
60
80
100
120
0
60
120
180
240
300
360
TIME (min)


A2 (17 ppb SO2)
A1 (no SO2)
A3
A5 (790 ppb SO2)
EXP
CMAQ
CHIMERE
O3 (ppb)
TIME (min)
0
60
120
180
240
300
200
400
600
800

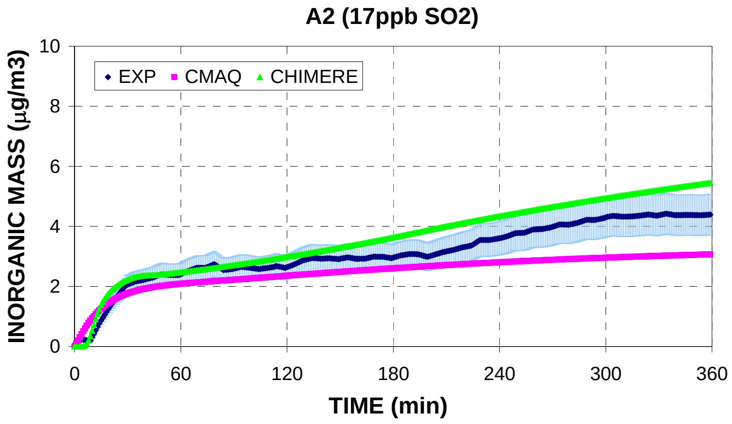

A2 (17 ppb SO2)
MON
CMAQ
CHIMERE
SO2 (ppb)
0
10
20
30
40
50
0
60
120
180
240
300
360
TIME (min)


A3 (514 ppb SO2)
FTIR
MON
CMAQ
CHIMERE
SO2 (ppb)
0
200
400
600
800
0
60
120
180
240
300
TIME (min)

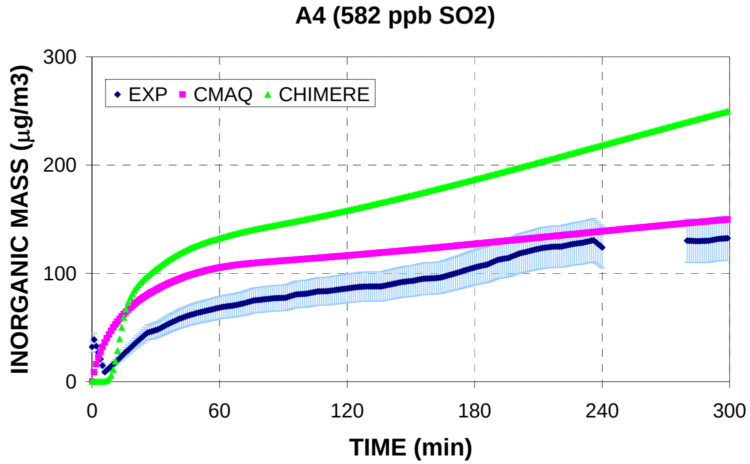

A4 (582 ppb SO2)
FTIR
MON
CMAQ
CHIMERE
SO2 (ppb)
0
200
400
600
800
0
60
120
180
240
300
TIME (min)


A5 (790 ppb SO2)
MON
FTIR
CMAQ
CHIMERE
SO2 (ppb)
500
700
900
1100
0
60
120
180
240
300
TIME (min)

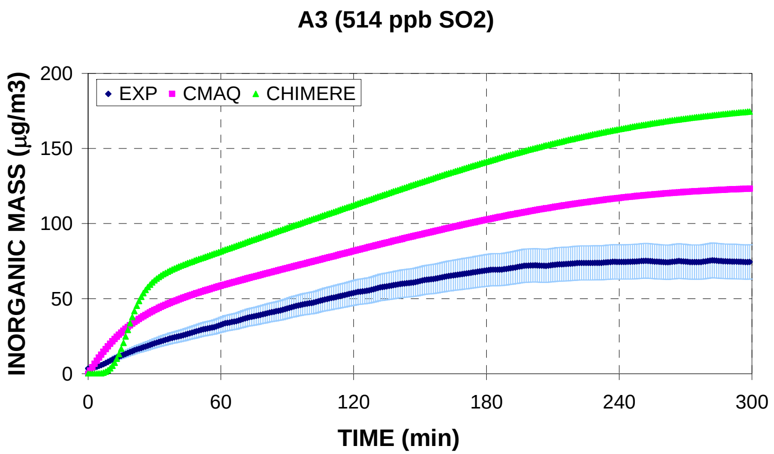
# *Results for the aerosol phase:*
# *sulphates and nitrates*



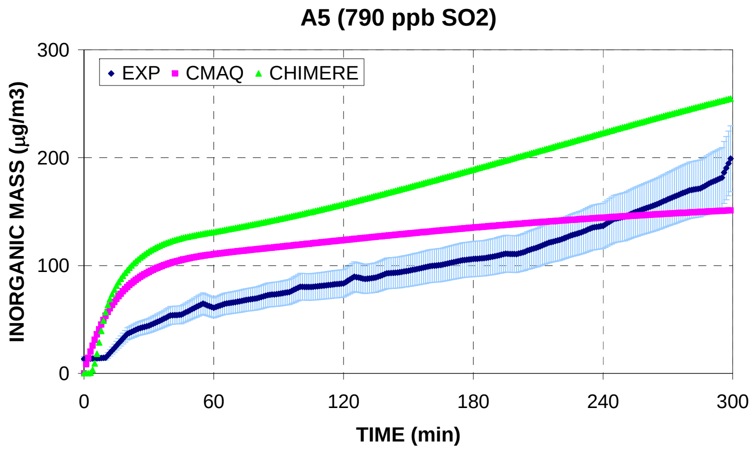
A2 (17ppb SO2)
INORGANIC MASS (µg/m3)
EXP CMAQ CHIMERE
TIME (min)

A4 (582 ppb SO2)
INORGANIC MASS (µg/m3)
EXP CMAQ CHIMERE
TIME (min)

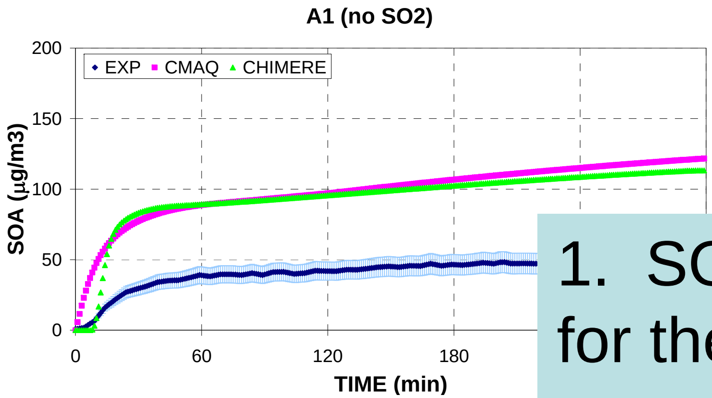



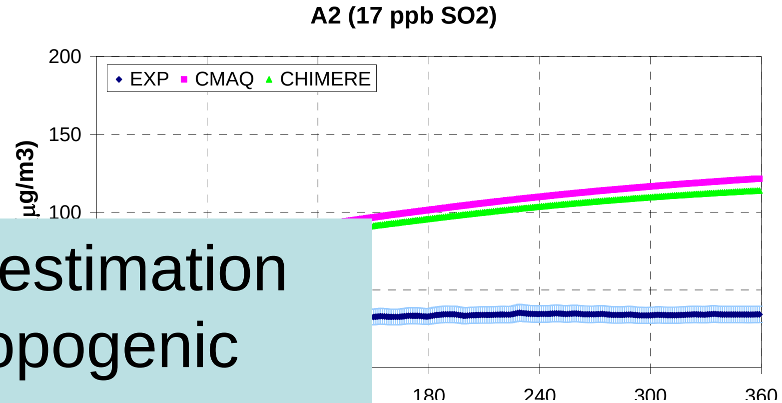
A3 (514 ppb SO2)
INORGANIC MASS (µg/m3)
EXP CMAQ CHIMERE
TIME (min)

A5 (790 ppb SO2)
INORGANIC MASS (µg/m3)
EXP CMAQ CHIMERE
TIME (min)

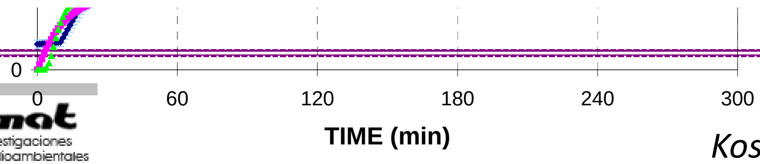
# *Results for the aerosol phase: organic aerosols*



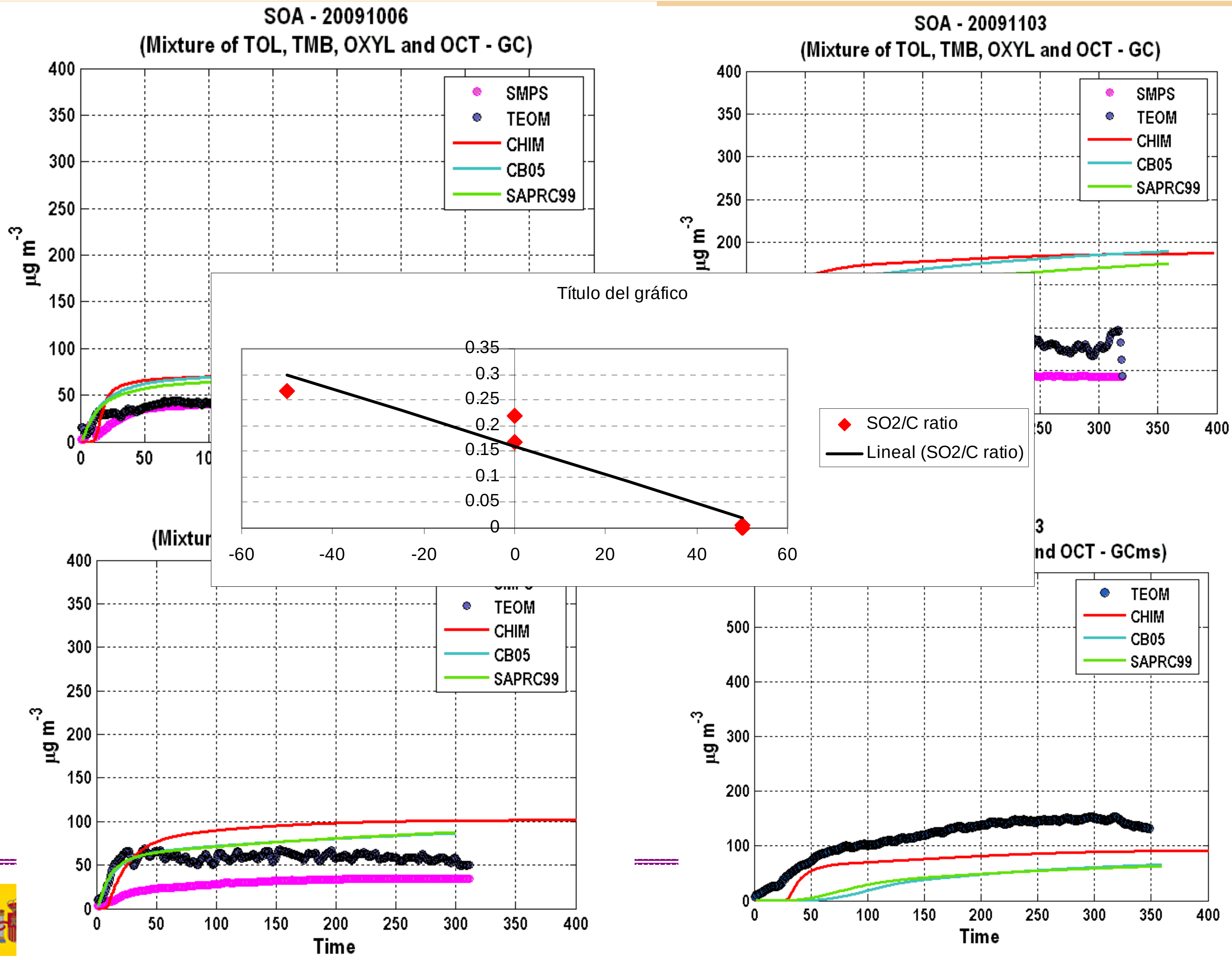




1. SOA overestimation for the anthropogenic precursors

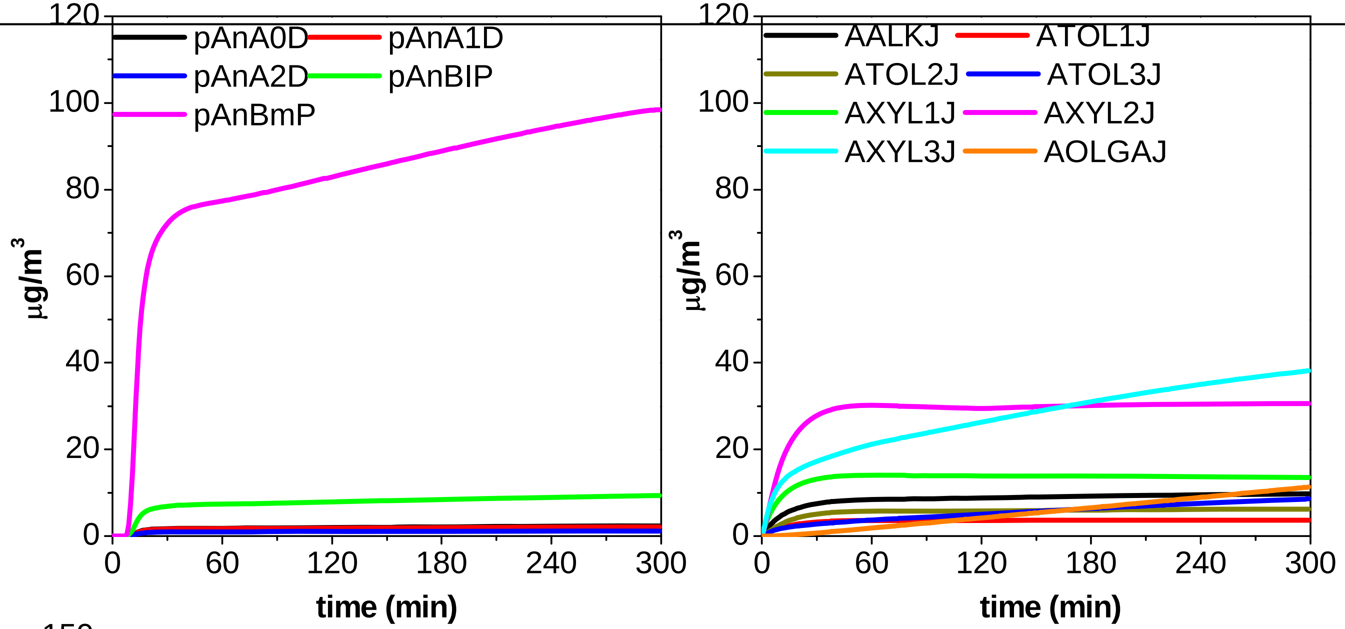
2. SOA acidic enhancement is not captured by any model. Large underestimation

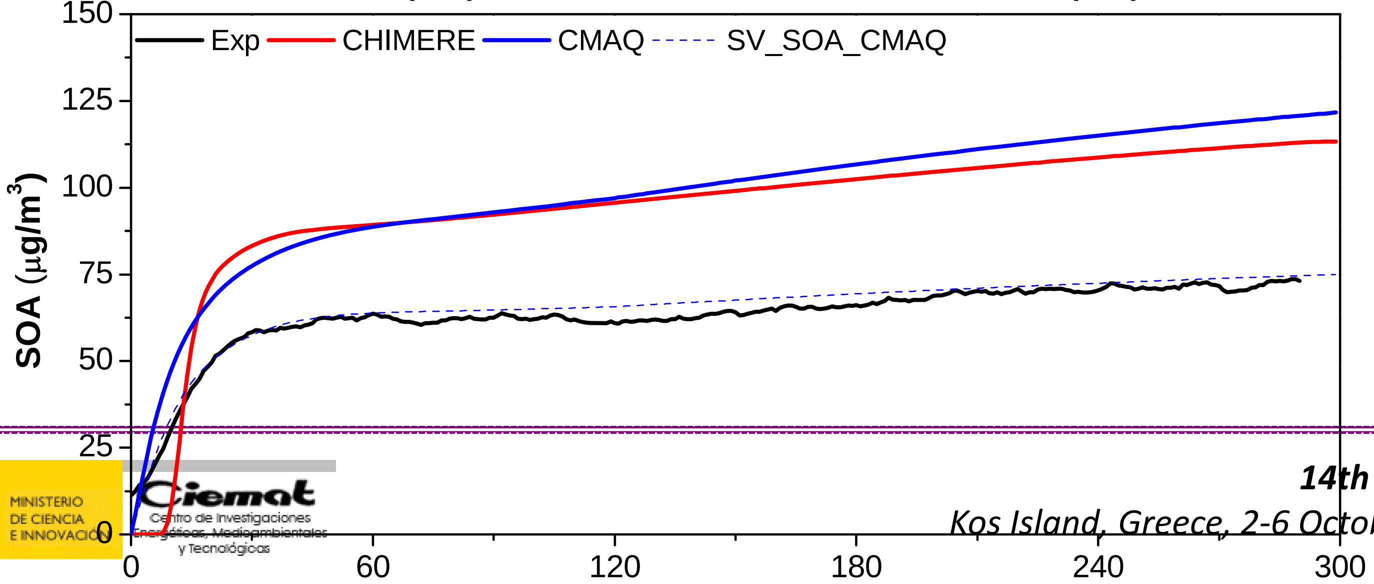


# RESULTS FOR AEROSOLS



*M. Santiago, Marta G. Vivanco ,and Ariel F. Stein, 2011. Secondary Organic Aerosol Modelization in Air Quality Models*

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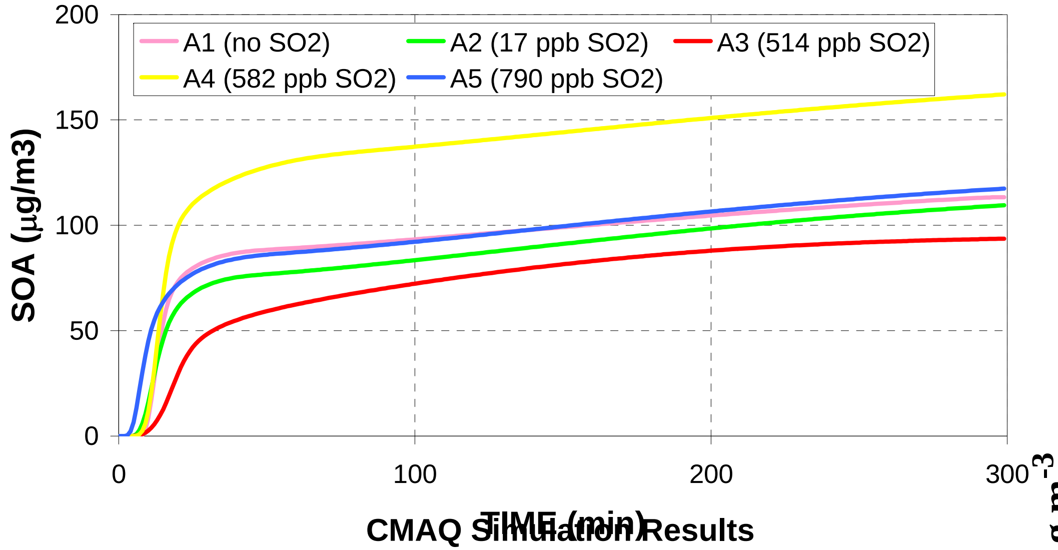
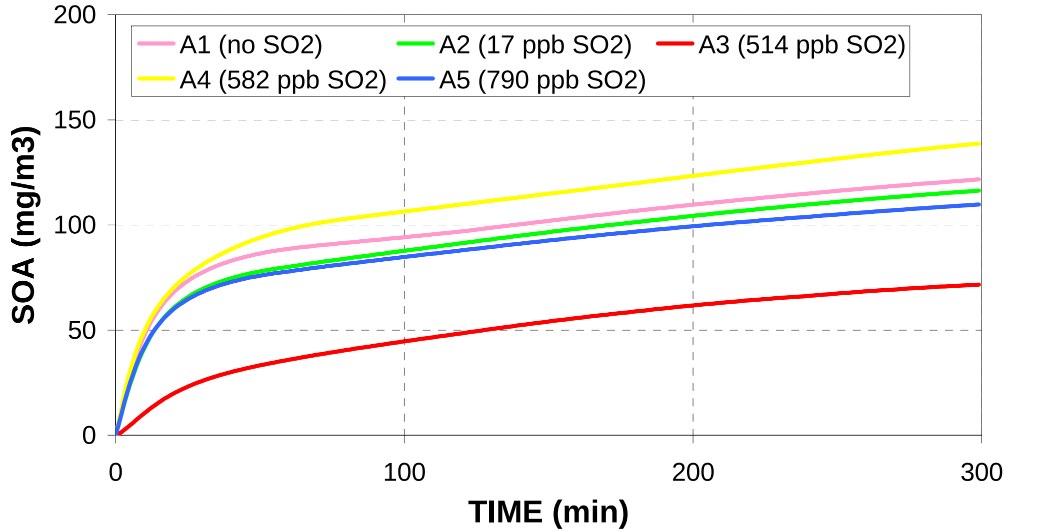
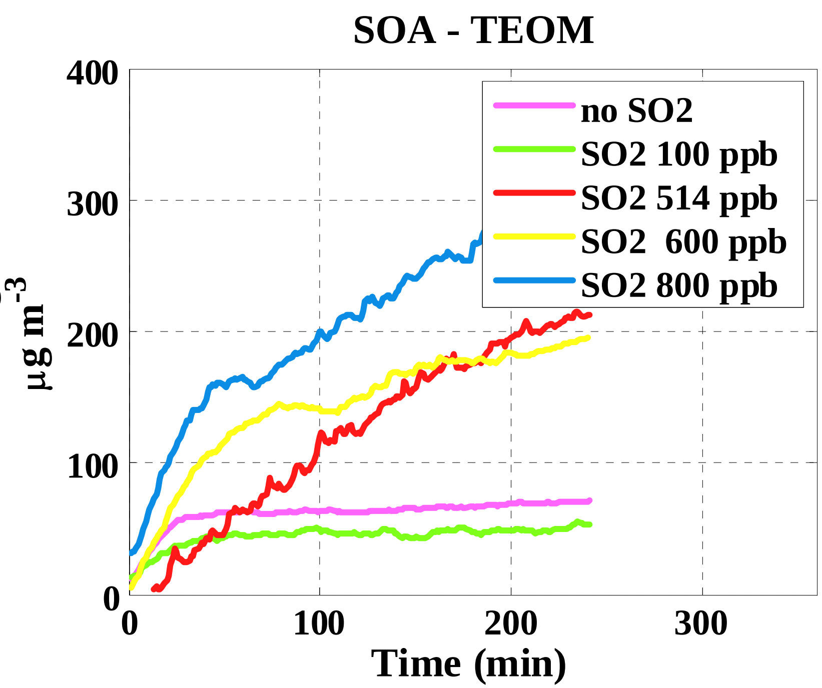
## CHIMERE Simulation Results




## CMAQ Simulation Results



| | ppbC | ppb SO2 | ppbC/ppb SO2 |
|---|---|---|---|
| 20080617 (A1) | 3150 | 0 | |
| 20080701 (A2) | 3109 | 17 | 183 |
| 20091116 (A3) | 2352 | 514 | 5 |
| 20100608 (A4) | 3458 | 582 | 6 |
| 20080626 (A5) | 2967 | 790 | 4 |

**La Coruña**

| | |
|---|---|
| ppbC/ppbSO2 | 6 |
| ppbC_tot/ppbSO2 | 9 |

**Osaka**

| | |
|---|---|
| ppbC/ppbSO2 | 29 |
| ppbC_tot/ppbSO2 | 50 |

# THANK YOU VERY MUCH!!

## ACKNOWLEDGEMENTS

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