Using the O_3/NOy Ratio to Assess the O_3-NOx-VOC Sensitivity in a Western Mediterranean Coastal Environment

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Case 1

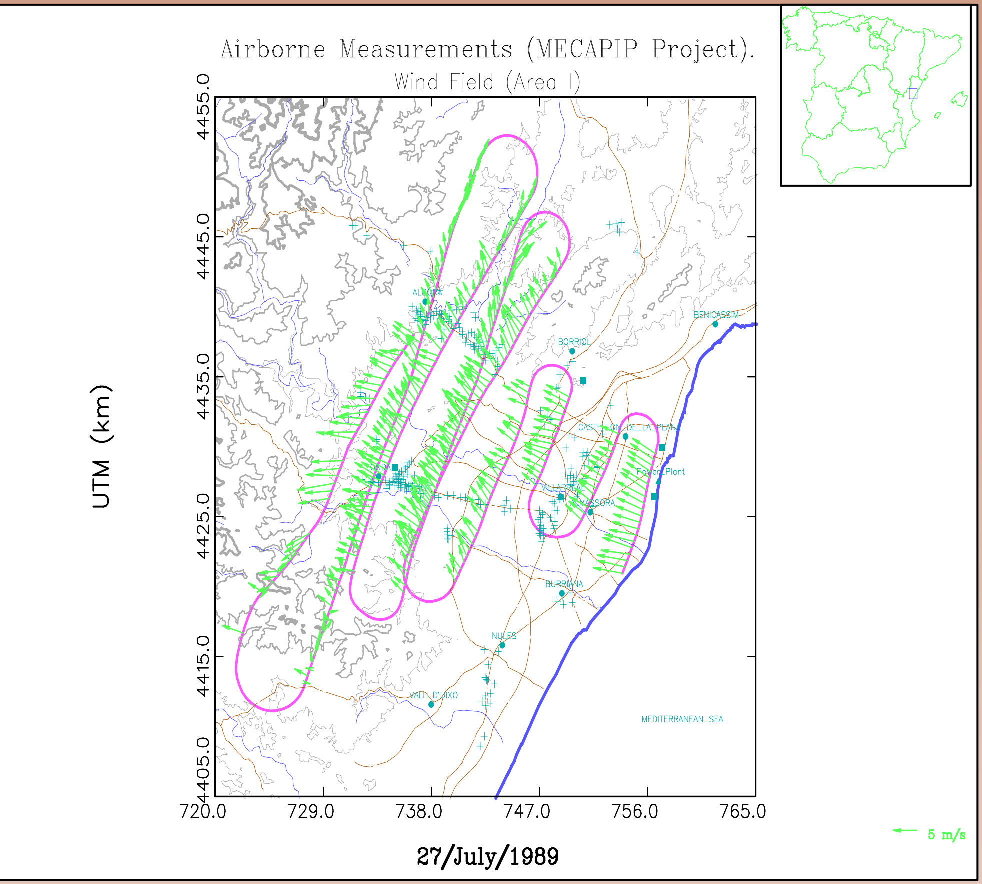
July 27, 1989

Castellon urban-industrial complex

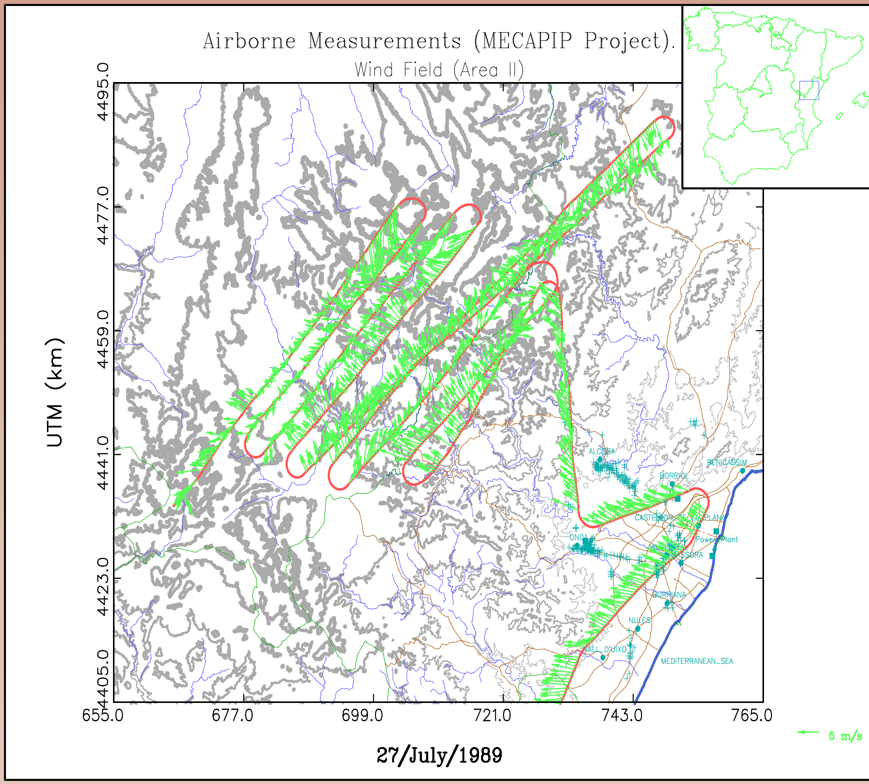
Western Mediterranean coast

Mesometeorological Cycles of Air Pollution in the Iberian Peninsula (MECAPIP) project

Flight patterns
(Hawker Siddeley 125 F400B)

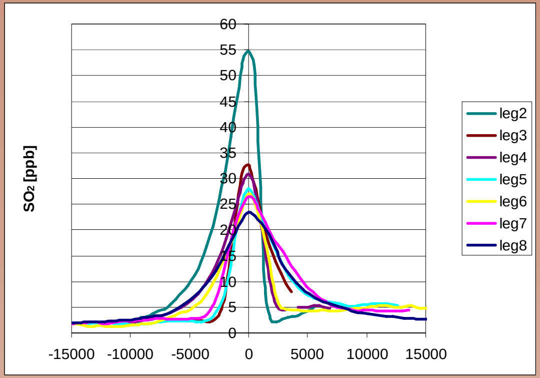


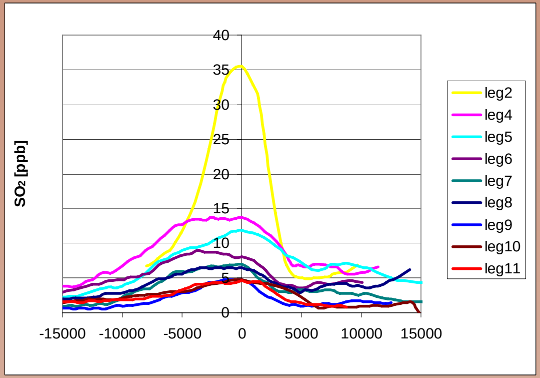
11:42 to 12:23 UTC

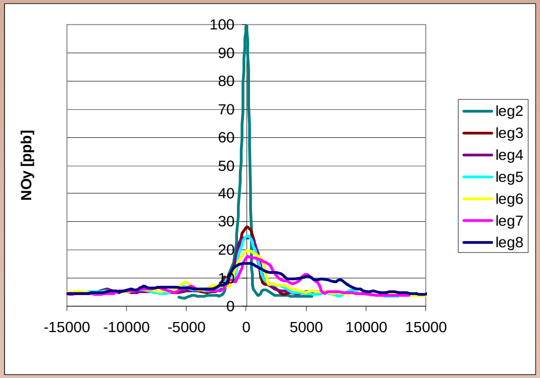


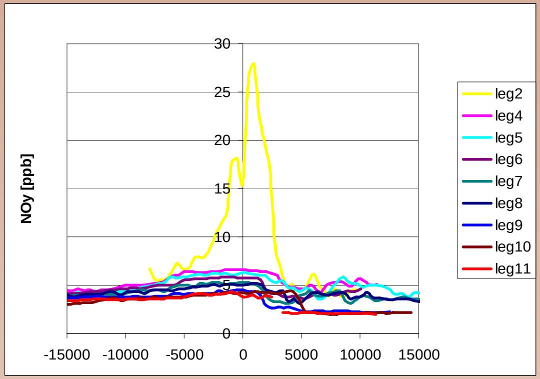
15:09 to 15:55 UTC

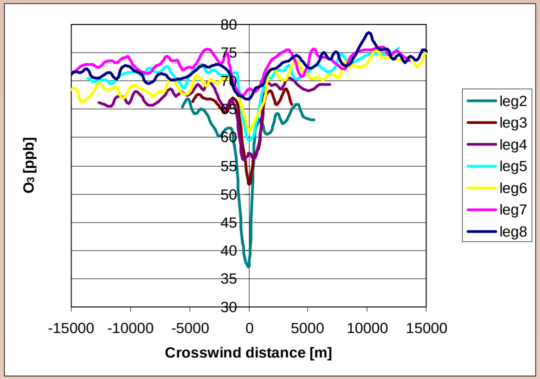
SO_2, NOy, and O_3 measurements

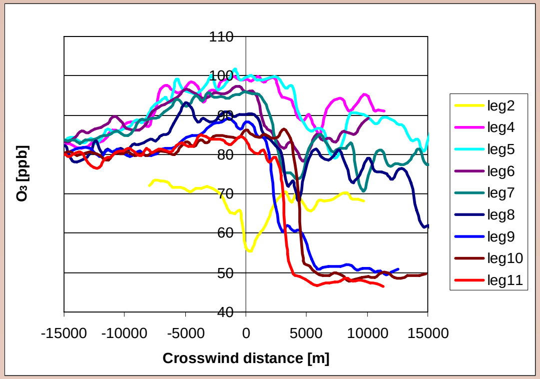






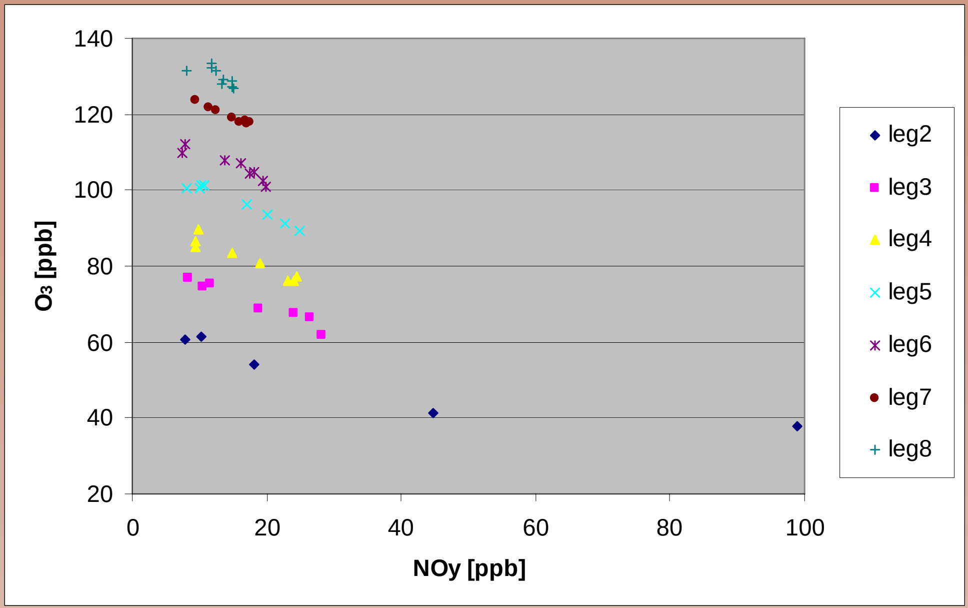




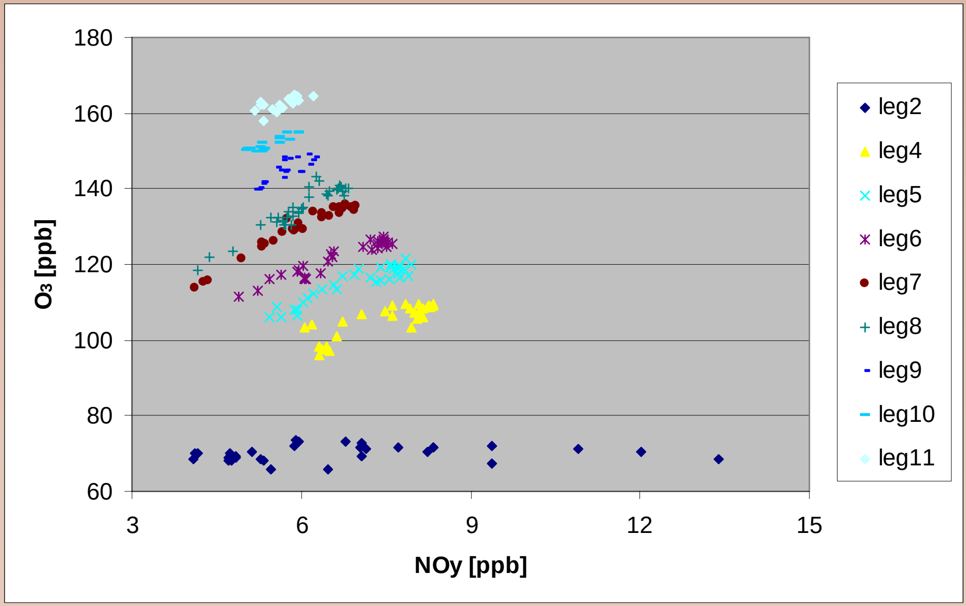


O_3 vs NOy

Morning



Afternoon

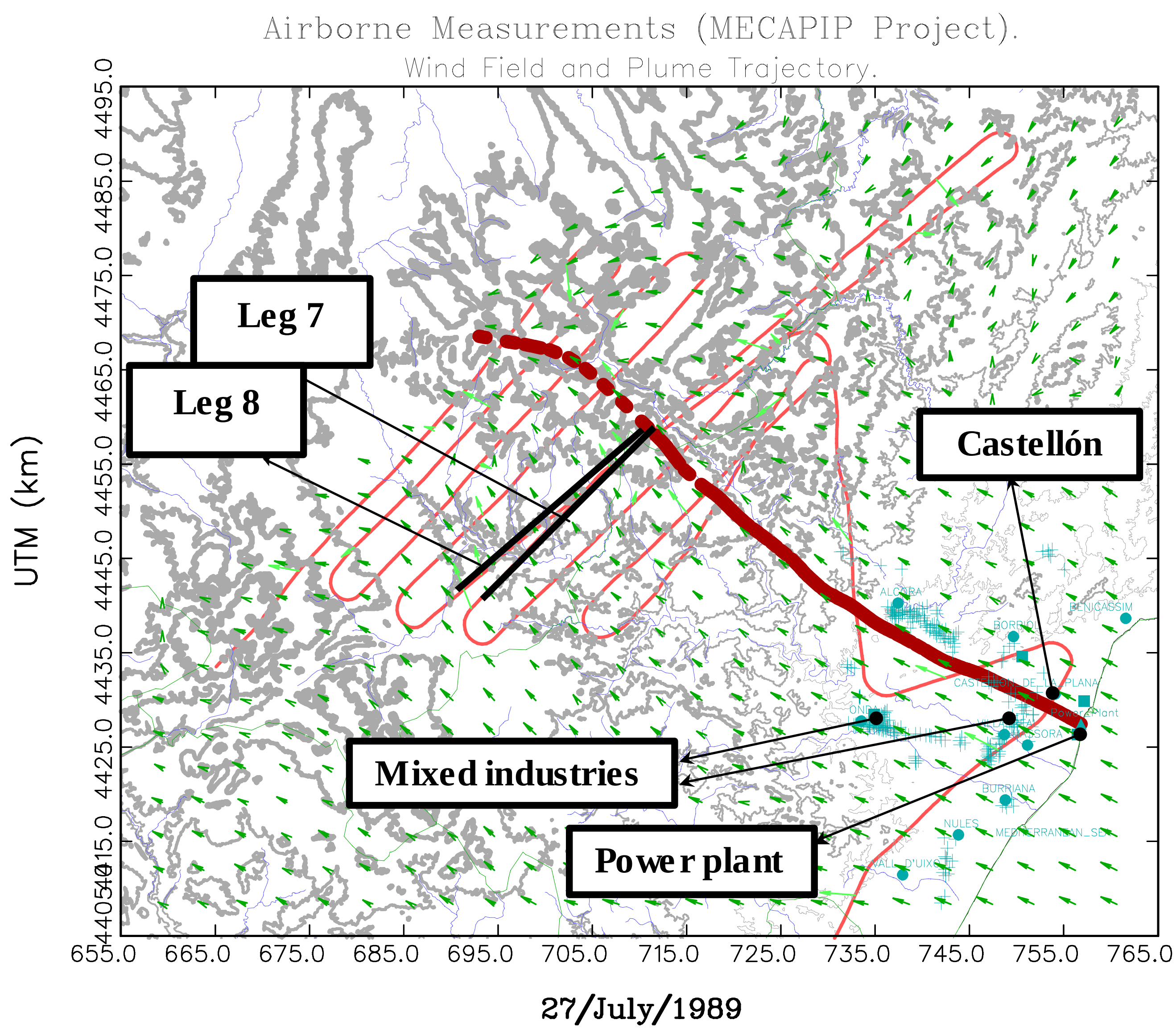


Meteorological conditions

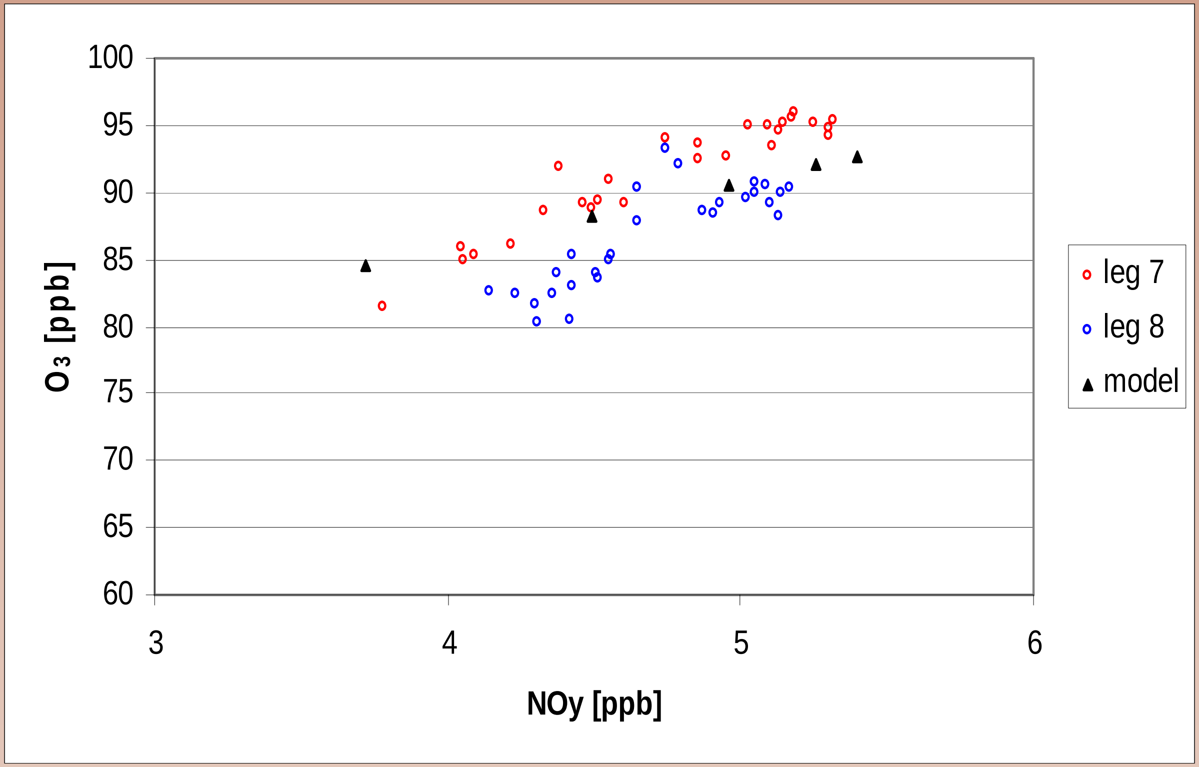
- Associated to an Atlantic high-pressure system, well established at mid-latitudes and extending to central Europe and the Western Mediterranean.
- Pollutants measured during the flights are emitted into an atmosphere relatively confined by the presence of at least one inversion layer.
- Wind field pattern shows a well-defined easterly circulation

Reactive Plume Model (RPM-IV) description

- Lagrangian approach to describe a horizontally segmented air parcel as it moves downwind
- 5 horizontal segments, starting width 1 km
- Chemistry: CB-IV
- Emissions: local inventory (mobile, area and industrial sources) and biogenic
- Initial conditions: morning flight
- Boundary conditions: box model run w/o emissions


Airborne Measurements (MECAPIP Project).
Wind Field and Plume Trajectory.
UTM (km)
4495.0
4485.0
4475.0
4465.0
4455.0
4445.0
4435.0
4425.0
4415.0
655.0
665.0
675.0
685.0
695.0
705.0
715.0
725.0
735.0
745.0
755.0
765.0
27/July/1989
Leg 7
Leg 8
Castellón
Mixed industries
Power plant
ALCORA
BENICASSIM
BORRIOL
CASTELLON_DE_LA_PLANA
BURRIANA
NULES
MEDITERRANEAN_SEA
VALL_D'UIXO

Model vs. Measurements



	BASE	
	O_3	***NOy***
Minimum[ppb]	84.5	3.7
Maximum[ppb]	92.7	5.4
Bias (min) [ppb]	-4.2	0.1
Norm Bias (min) [%]	-5.2	1.7
Bias (max) [ppb]	3.2	-0.1
Norm Bias (max) [%]	3.4	-1.5

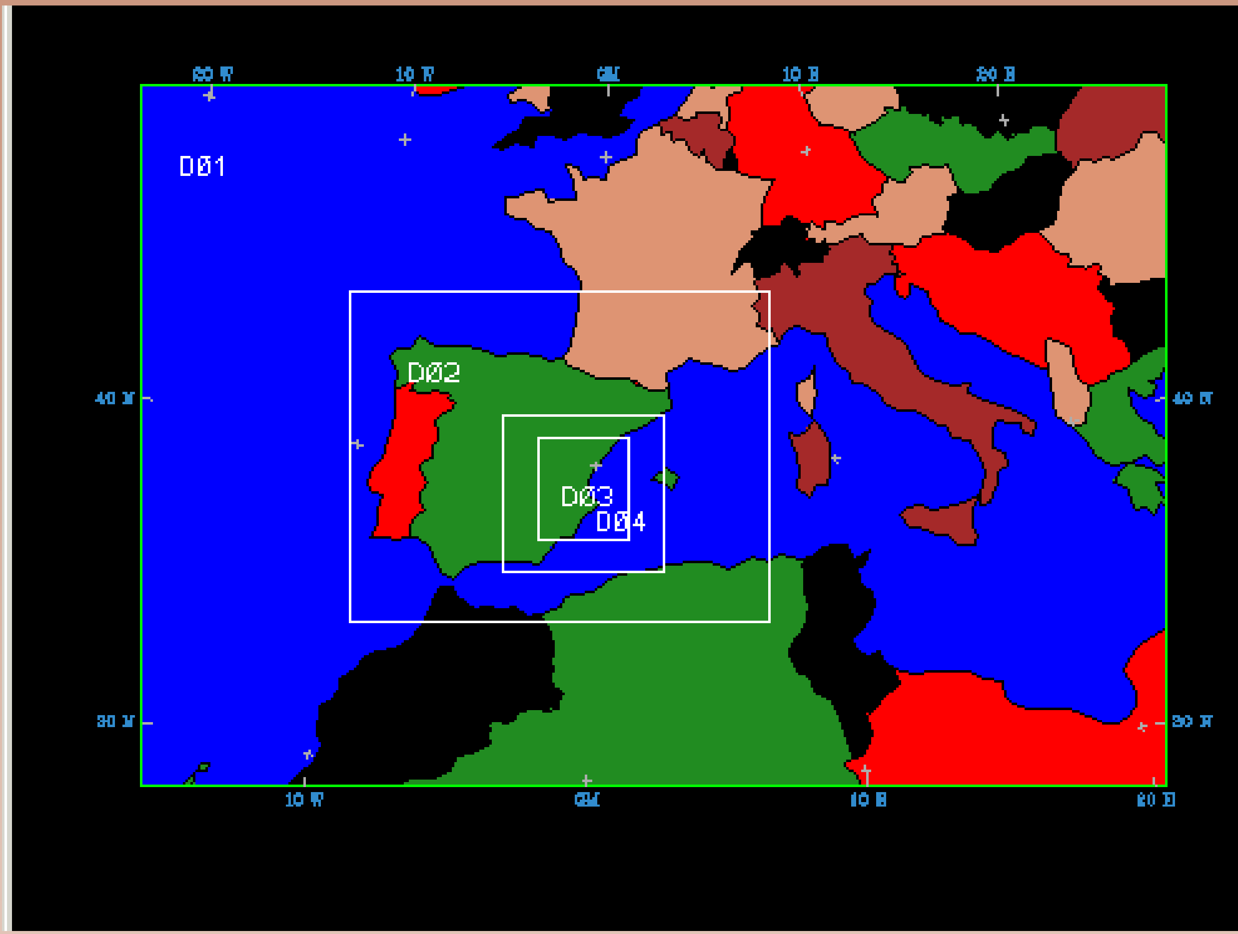
Case 2

August 14, 2000

Valencia Community

Western Mediterranean coast

MM5

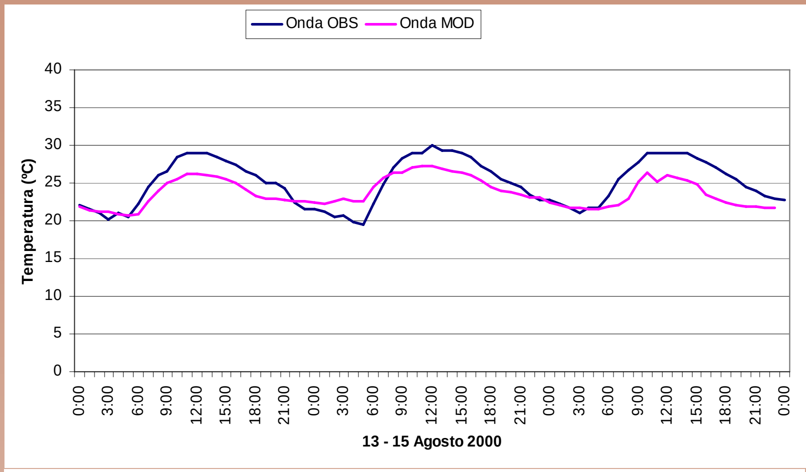


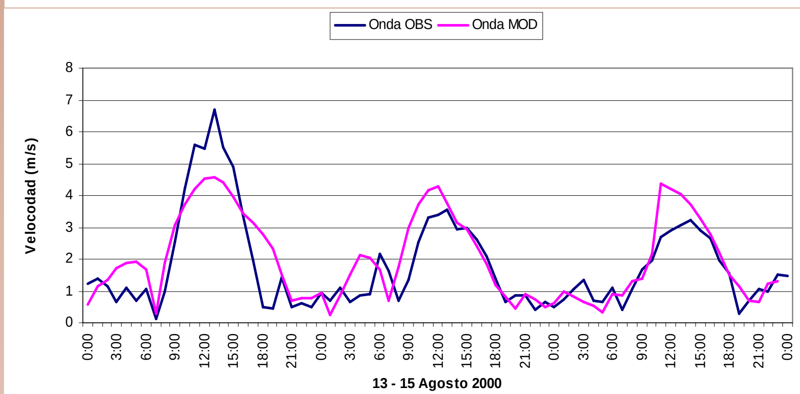
- Mellor and Yamada PBL
- Anthes-Kuo cumulus
- One-Way nestig
- NATLAN, 2000 land use data
- ECMWF initial conditions

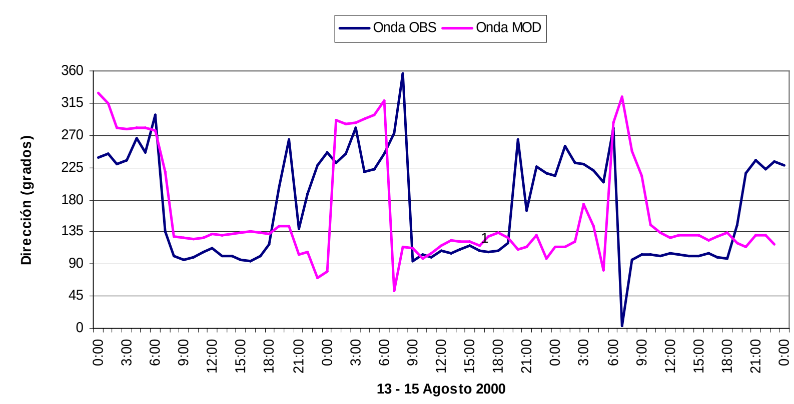
Grid	#X cells	# cells Y	# cells Z	Δ x (km)	Δ y (km)	Δ z (m) (lowest)	Δ t (s)
1	35	50	29	72	72	10	216
2	49	61	29	24	24	10	72
3	93	93	29	6	6	10	18
4	178	157	29	2	2	10	6

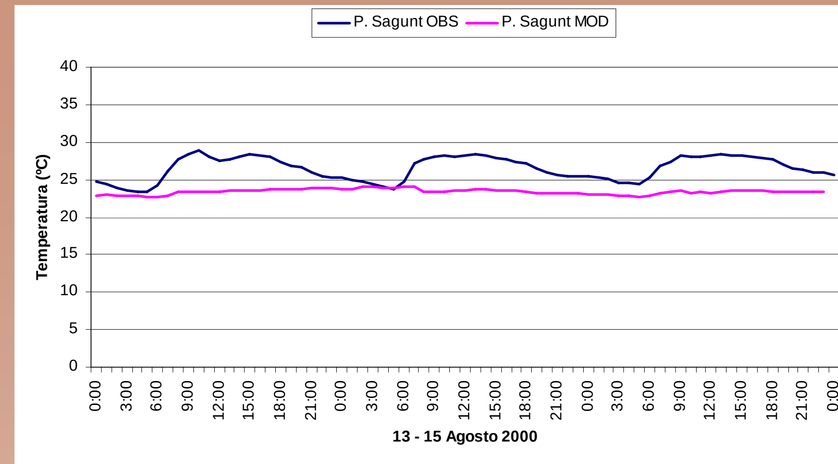
ONDA

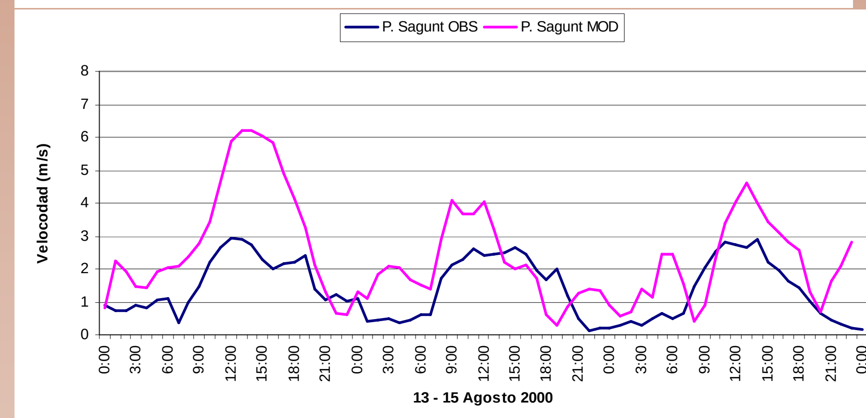
PORT SAGUNT

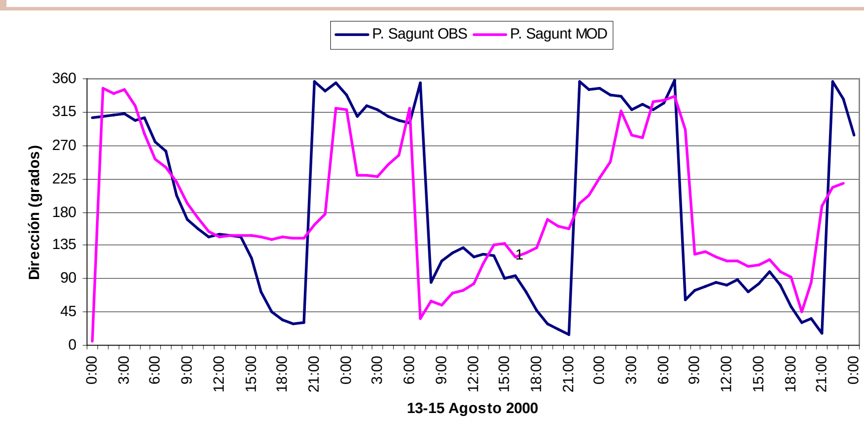






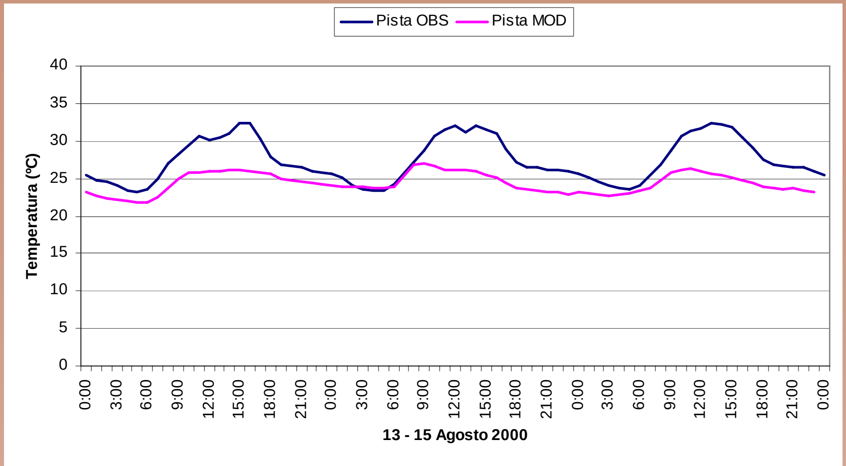


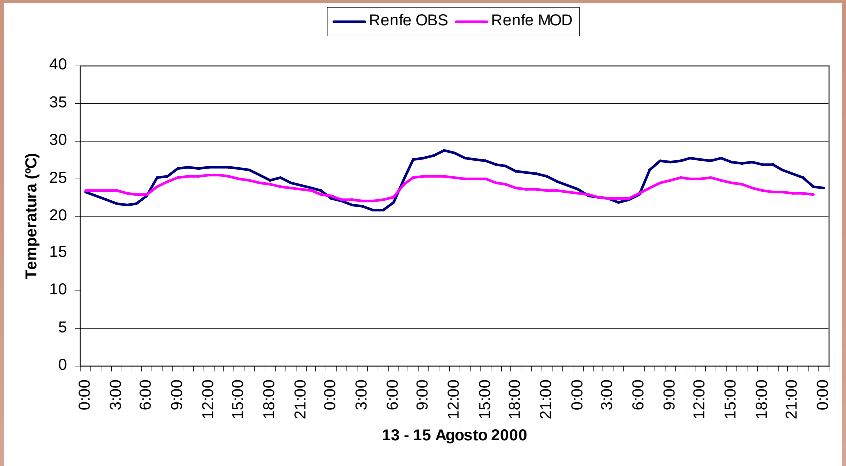


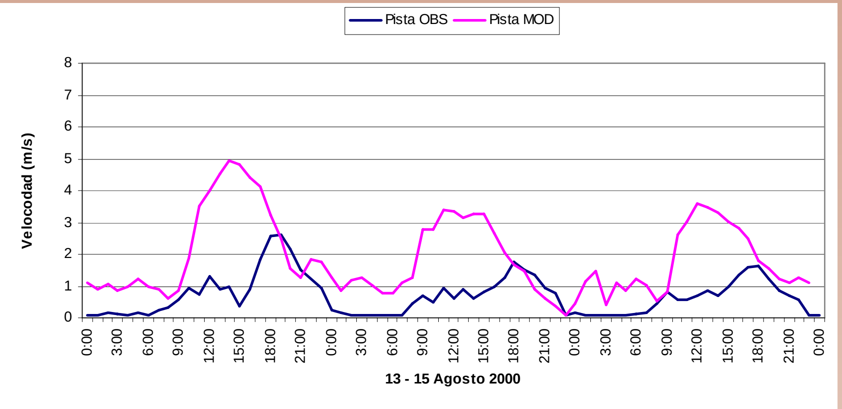


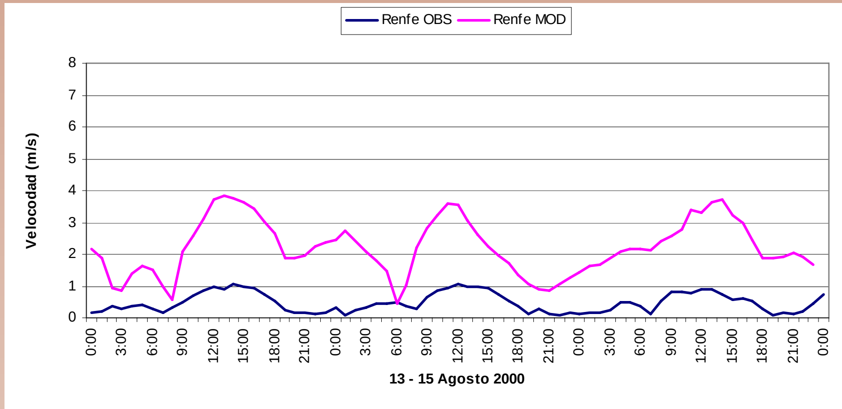
PISTA

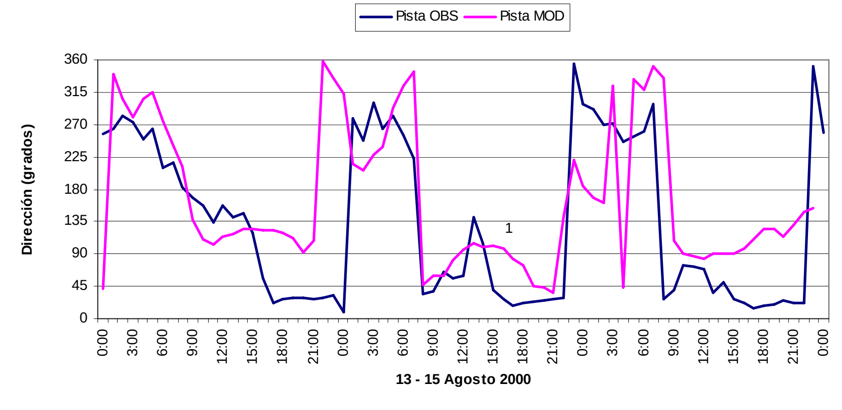
RENFE

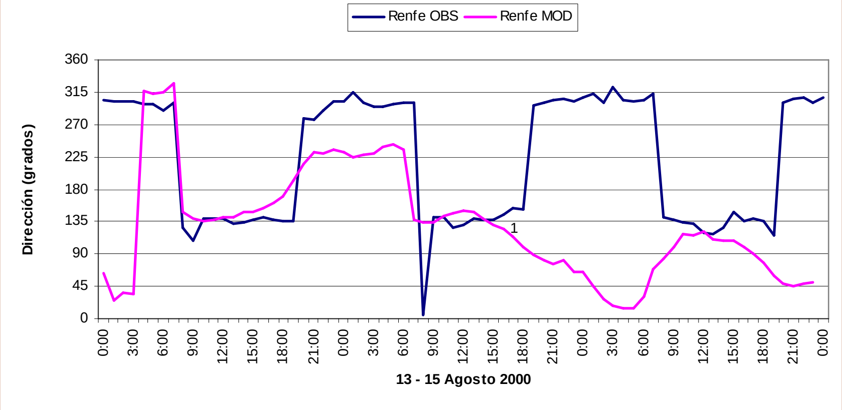

Pista OBS
Pista MOD
Temperatura (ºC)
13 - 15 Agosto 2000


Renfe OBS
Renfe MOD
Temperatura (ºC)
13 - 15 Agosto 2000


Pista OBS
Pista MOD
Velocidad (m/s)
13 - 15 Agosto 2000


Renfe OBS
Renfe MOD
Velocidad (m/s)
13 - 15 Agosto 2000


Pista OBS
Pista MOD
Dirección (grados)
13 - 15 Agosto 2000


Renfe OBS
Renfe MOD
Dirección (grados)
13 - 15 Agosto 2000

Emission sources

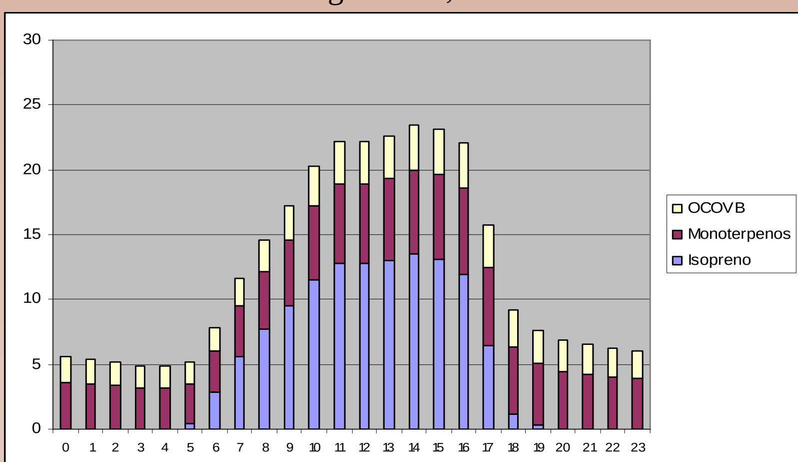
Biogenic Emissions

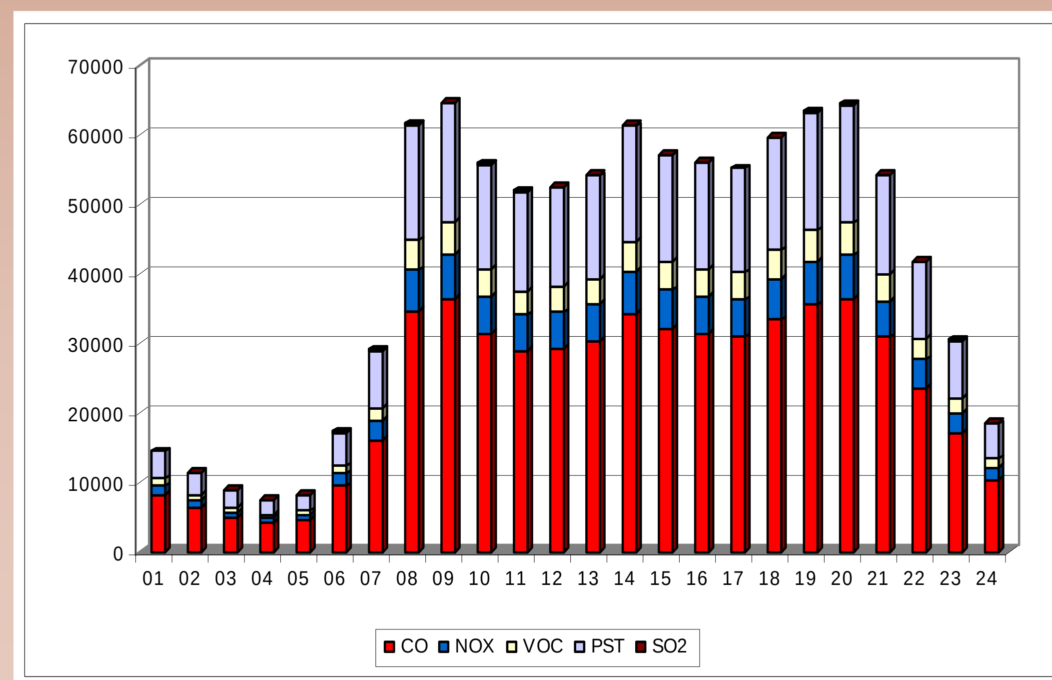
- Land use data
- Biomass factors by land use type
- Emission factors
- Meteorological data (T, PAR)

Trafic Emissions

- Geographical distribution and classification of roads
- VMT (vehicle miles traveled) data
- Chemical speciation for differnent kinds of vehicles
- Hourly profiles

August 13th, 2000

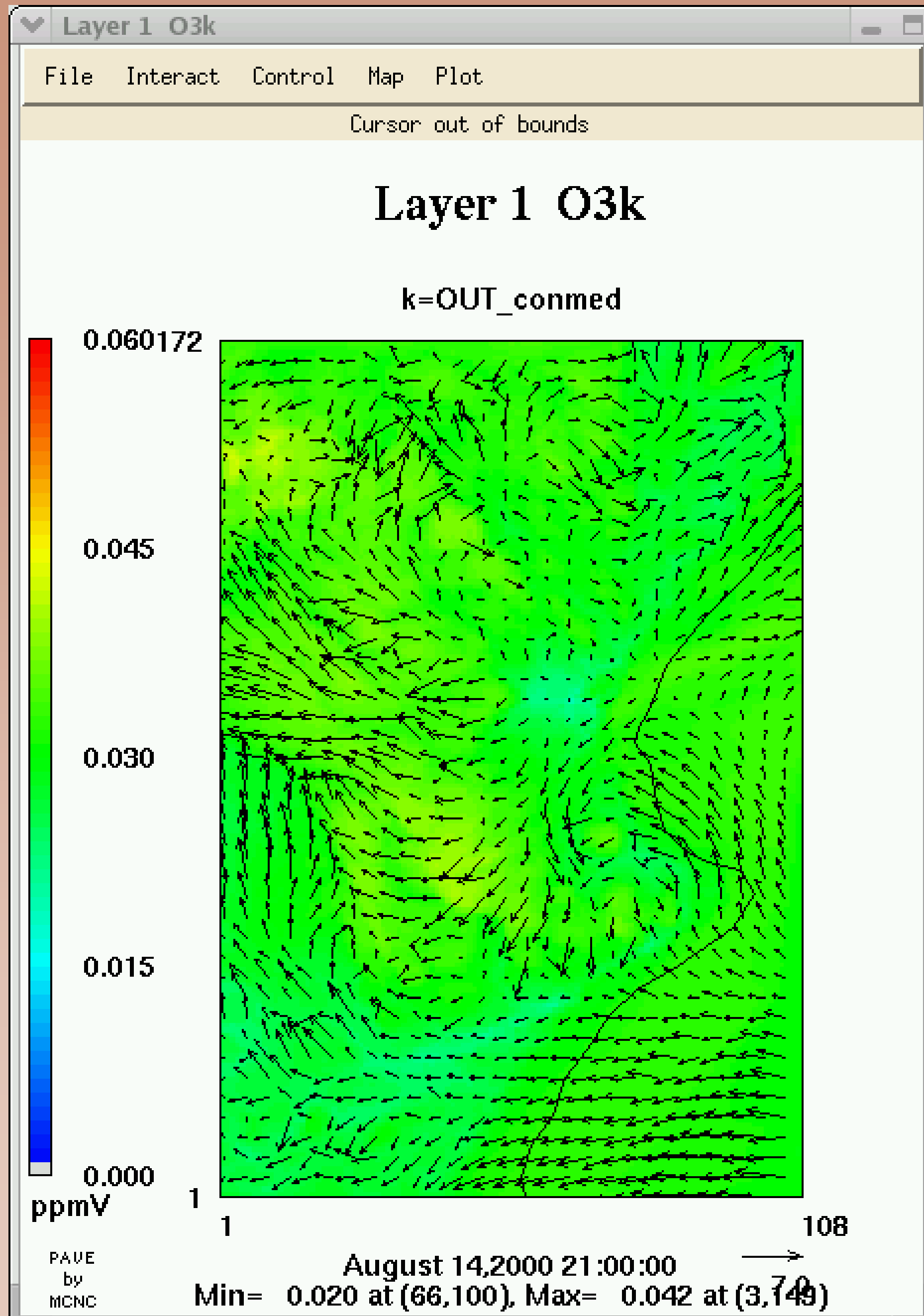




Weekday daily cicle of primary emissions (Kg/h)

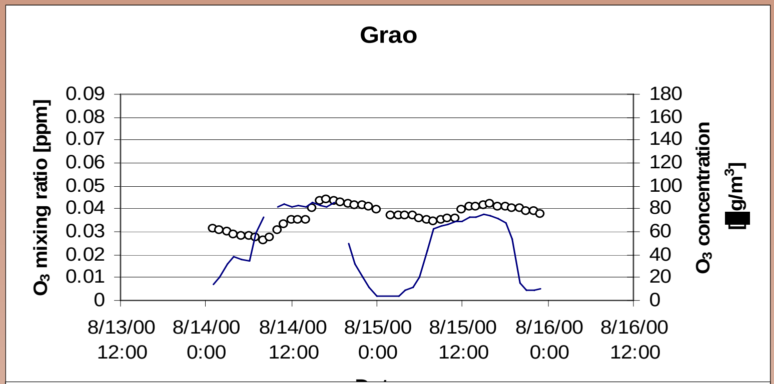
CMAQ

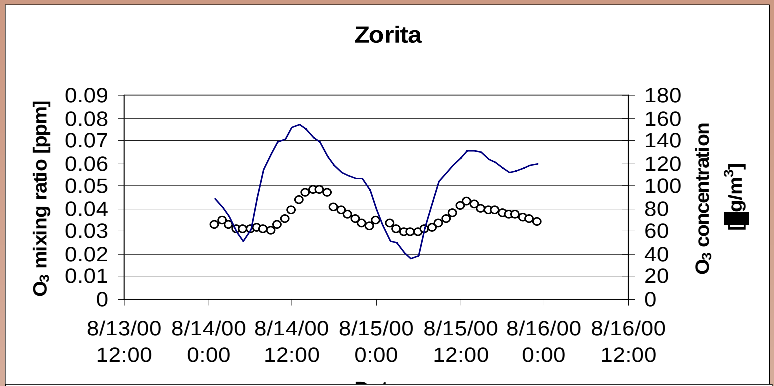
- Horizontal: 2 nests - 12 and 4 km
  - Domain 1: Iberian peninsula
  - Domain 2: Valencia Community
- Vertical: 15 layers - sigma p
- Chemical mechanism: Carbon Bond IV
- Meteorology preprocessor: Meteorological Chemistry Interface Processor (MCIP)
- Advection: pierce-wise parabolic method (PPM)
- Vertical diffusion: K-theory parameterization
- Gas-phase reaction solver: quasi-steady state approximation (QSSA)

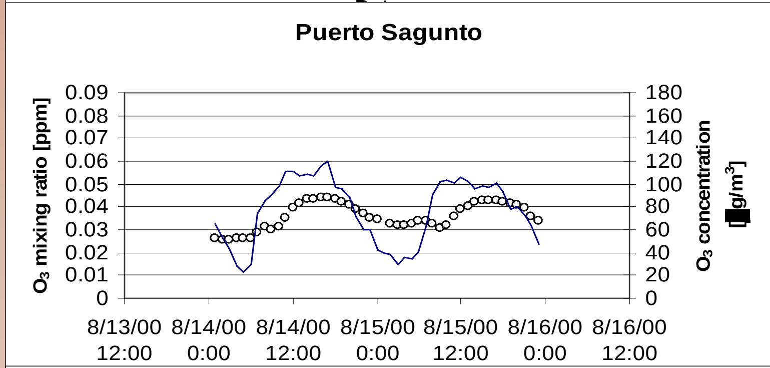


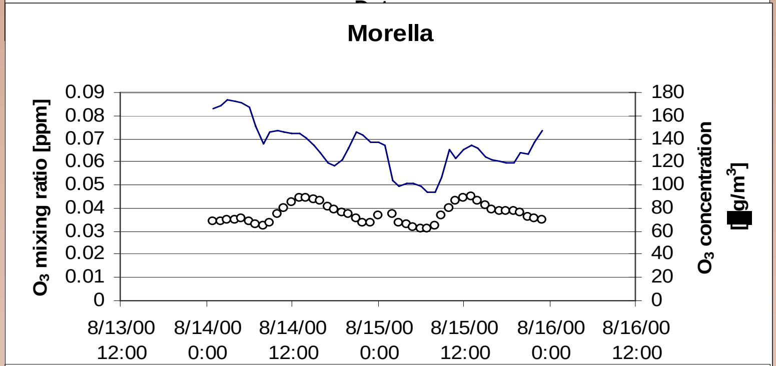
Layer 1 O3k
File Interact Control Map Plot
Cursor out of bounds
Layer 1 O3k
k=OUT_conmed
0.060172
0.045
0.030
0.015
0.000
ppmV
1
1
108
7.0
August 14,2000 21:00:00
Min= 0.020 at (66,100), Max= 0.042 at (3,149)
PAVE
by
MCNC

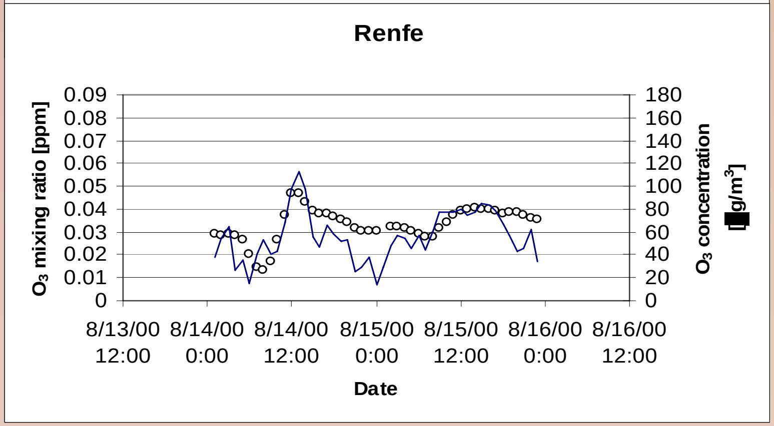
Model performance

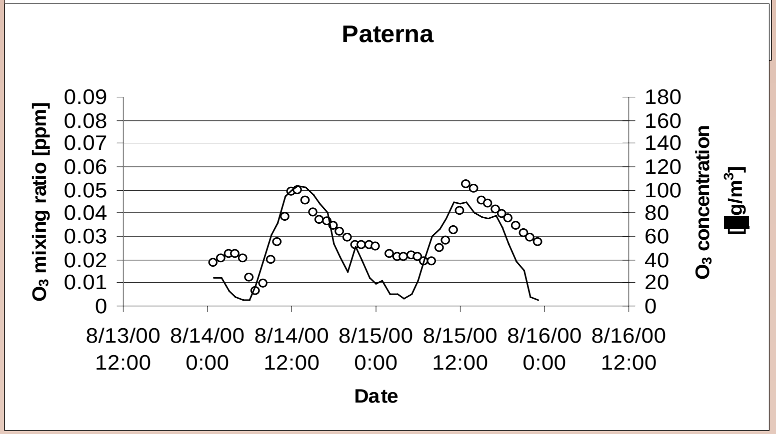


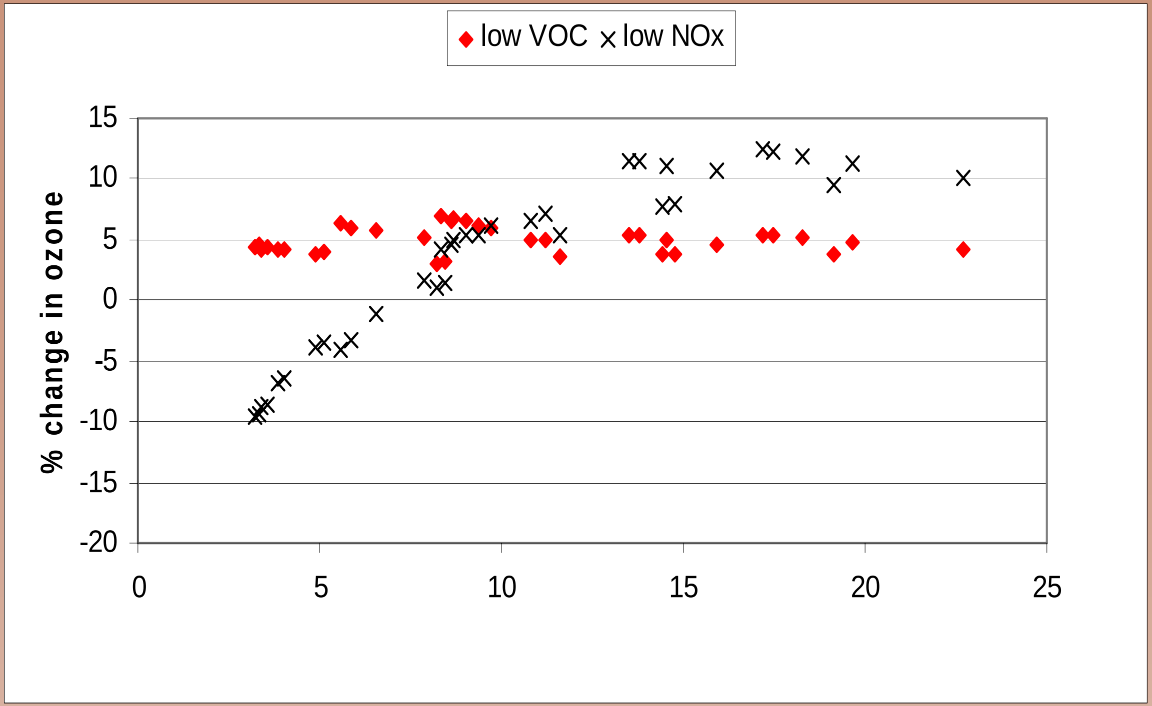






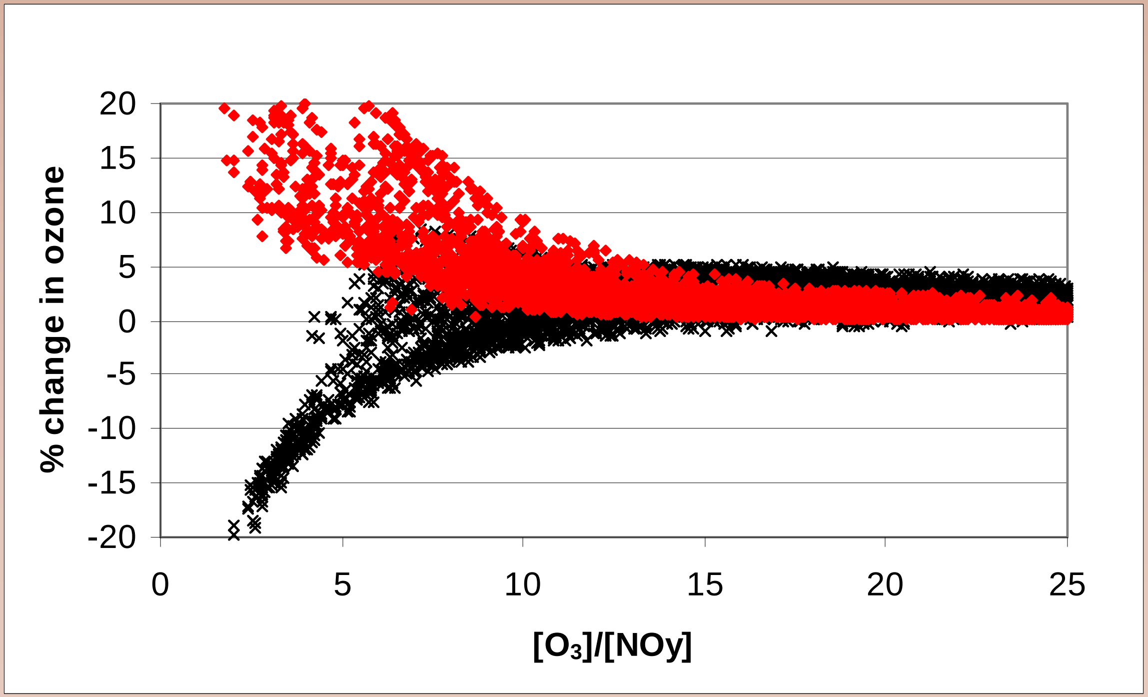






low VOC
low NOx
% change in ozone
15
10
5
0
-5
-10
-15
-20
0
5
10
15
20
25

Case 1



% change in ozone
20
15
10
5
0
-5
-10
-15
-20
0
5
10
15
20
25
$[O_3]/[NOy]$

Case 2

Indicator distribution

	VOC sensitive			**NOx sensitive**		
Percentile	5^{th}	50^{th}	95^{th}	5^{th}	50^{th}	95^{th}
O_3/NOy (**case 1**)	1.6	5.1	9.2	12.9	17.5	23.2
O_3/NOy (**case 2**)	3.3	8.2	12.5	12.9	26.1	53.6
NE corridor, USA (Sillman and He,2002)	5.0	5.4	6.5	8.2	12.7	18.0
Lake Michigan, USA (Sillman and He,2002)	3.5	5.2	6.6	7.2	11.7	16.0
Atlanta, USA (Sillman et al, 1997)	3.6	5.1	7.2	8.1	14.3	27.0
San Joaquin, USA (Sillman and He,2002)	3.0	7.3	11.6	15.0	26.0	56.0
Milan, Italy (Martilli et al., 2002)	3.6	4.3	5.6	5.7	8.2	11.1

Why the O_3/NOy transition is different in different environments?

- $O_3/NOz \sim [S_H/L_N]\ [L_N/NOz]\ [O_3/S_H]$
- L_N/NOz : relates to the removal rate of NOz
- O_3/S_H : more important
  - $S_H \sim O_3$ and VOC
  - higher VOC ==> lower O_3/S_H ==> lower transition
  - O_3/S_H also varies with photochemical age
- O3/NOy = $[O_3/NOz]\ [NOz/NOy]$

Summary

- 2 summertime cases analyzed for a Western Mediterranean coastal area.
- O_3/NOy threshold values for the transition between VOC- and NOx- O3-sensitivity higher than NE US.
- Higher threshold values due to:
    - lower ozone levels in Valencian Community (70-100 ppb)
    - uncertainty in regarding O_3/NOy as a surrogate to the ratio of the source of odd hydrogen to the source of odd nitrogen when calculating the ratios.