# *Phenomenology of ozone episodes in Spain*

**X. Querol[1], A. Alastuey[1], C. Carnerero[1], N. Pérez[1], J. Massagué[1], A. Canals[1], G. Gangoiti[2], L. Alonso[2], E.Mantilla[3], J.J.Diéguez[3], M.Escudero[4], M.Hervás[5], A.Campos[5], I.Olivares[5], M.BLarka[5], J.R.Moreta[6], M.Millán[3]**

*[1]Instituto de Diagnóstico Ambiental y Estudios del Agua (IDAEA-CSIC), Barcelona, Spain*

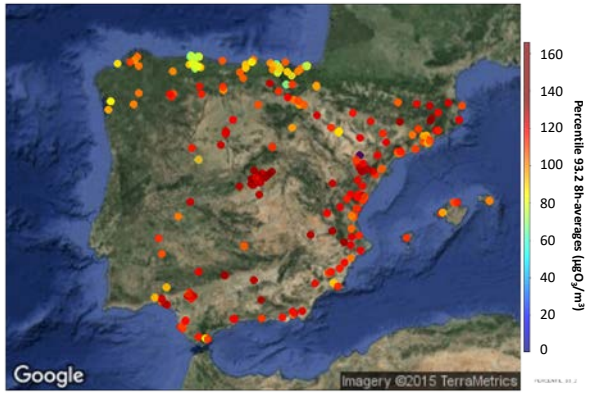
*[2]E.T.S. Ingeniería de Bilbao, Dpto. Ingeniería Química y del Medio Ambiente, Universidad País Vasco UPV/EHU, Bilbao, Spain*

*[3]Centro de Estudios Ambientales del Mediterráneo, CEAM, Unidad Asociada al CSIC, Valencia, Spain*

*[4]Centro Universitario de la Defensa de Zaragoza, Academia General Militar, Zaragoza, Spain*

*[5]D.G. Calidad y Evaluación Ambiental, Ministerio para la Transición Ecológica, Madrid, Spain*

*[6]Agencia Estatal de Meteorología, AEMET, Madrid, Spain*




***WORKSHOP ON AIR QUALITY POLICY IMPLEMENTATION RELATED TO OZONE***

***TAIEX-EIR PEER 2 PEER***

Ministry for the Ecological Transition, Madrid, 21-22 November 2018

# Outline

- $O_3$ in Spain and time trends
- Origin of $O_3$ episodes in three atmospheric basins

GOBIERNO DE ESPAÑA
MINISTERIO PARA LA TRANSICIÓN ECOLÓGICA

GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES

¡MADRID!
ÁREA DE GOBIERNO DE MEDIO AMBIENTE Y MOVILIDAD

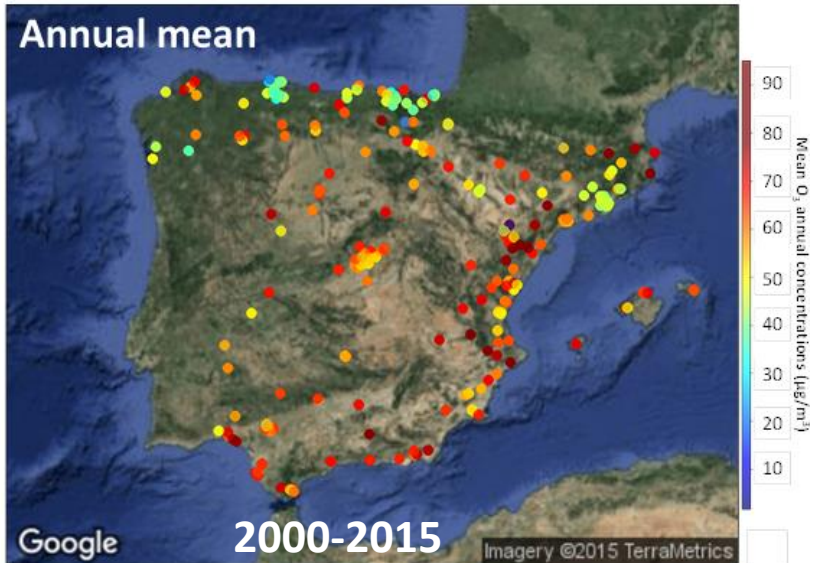
Generalitat de Catalunya
Departament de Territori i Sostenibilitat

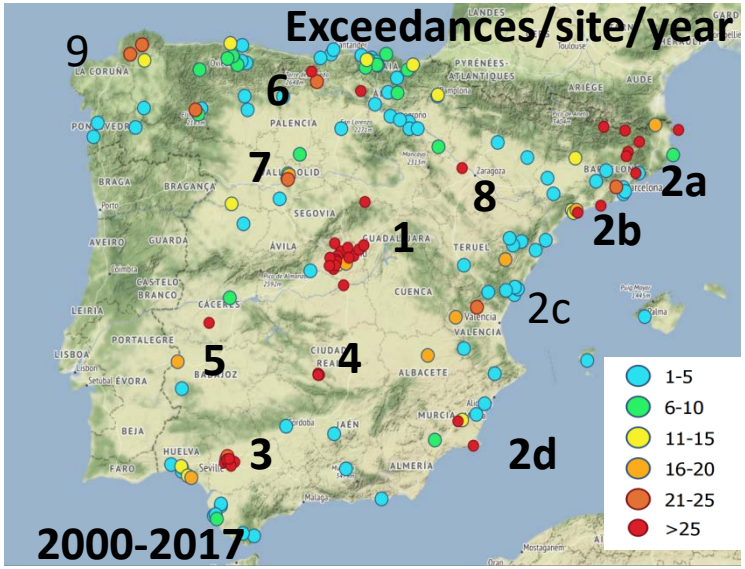
JUNTA DE ANDALUCIA

house.

HIGH OZONE, ULTRAFINE PARTICLES AND SECONDARY ORGANIC AEROSOLS
CGL2016-78594-R

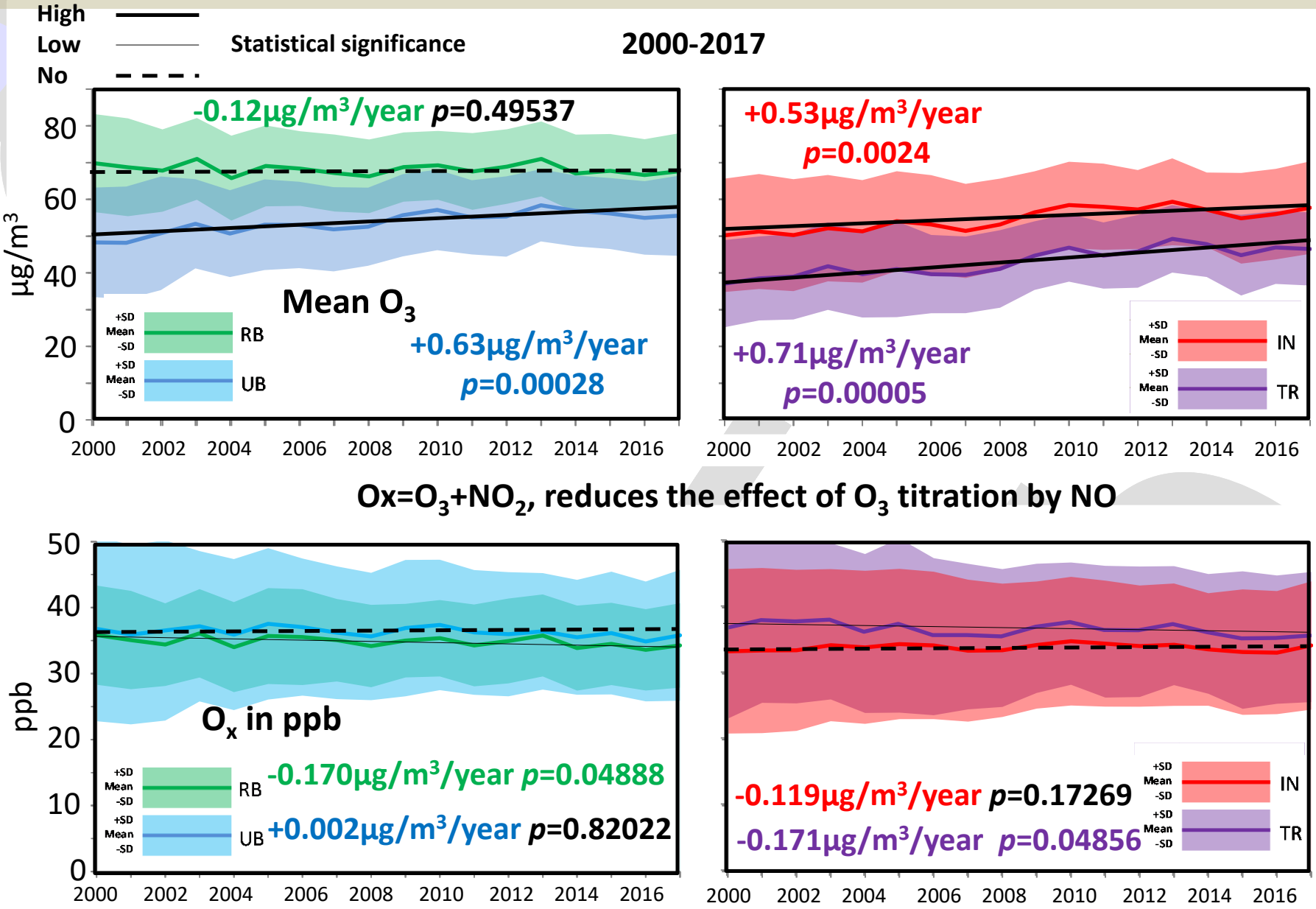
# Levels and time-trends of $O_3$ in Spain



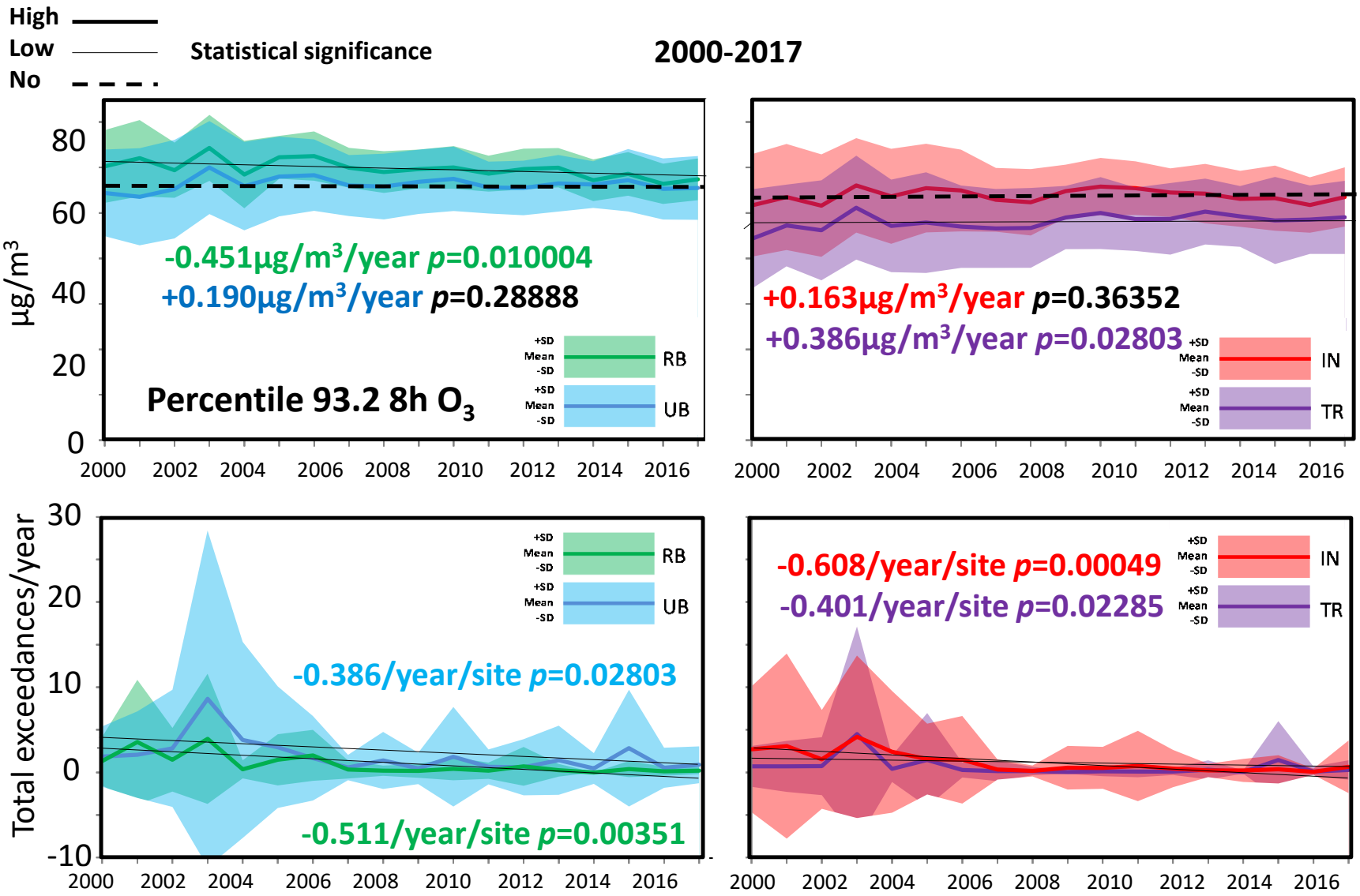

*Querol X. et al., Science of the Total Environment 572 (2016) 379–389*

# Levels and time-trends of $O_3$ in Spain




*Updated from Querol X. et al., Science of the Total Environment 572 (2016) 379–389*

# Levels and time-trends of $O_3$ in Spain



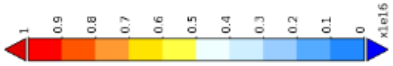

**Exceedances/year 180 µg/m³ 1 h $O_3$**

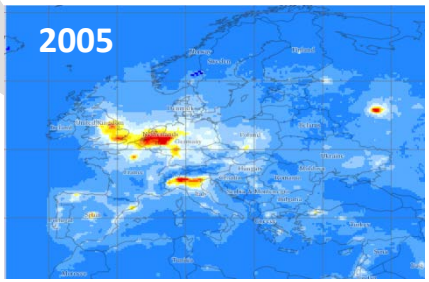
*Updated from Querol X. et al., Science of the Total Environment 572 (2016) 379–389*

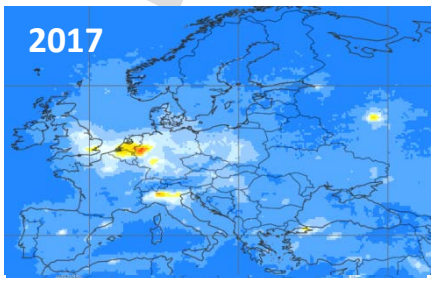
# Levels and time-trends of $O_3$ in Spain

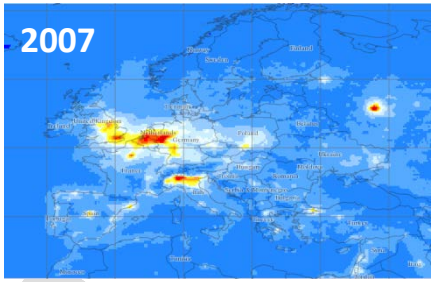
**NASA $NO_2$ OMI level 3** Plotted using the Giovanni online data system, developed and maintained by the NASA GES DISC

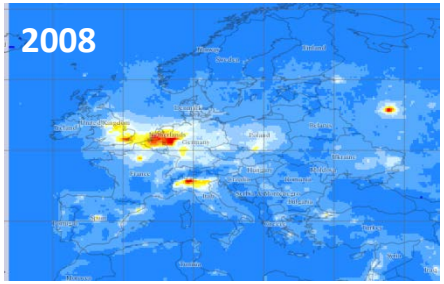
**Mean annual tropospheric $NO_2$ column** (clear, 0-30% cloud) **($10^{14}$ molec/cm$^2$)**

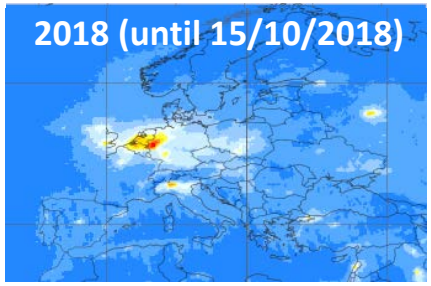


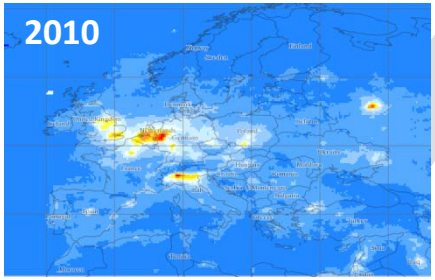



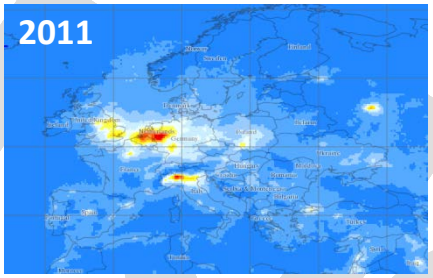



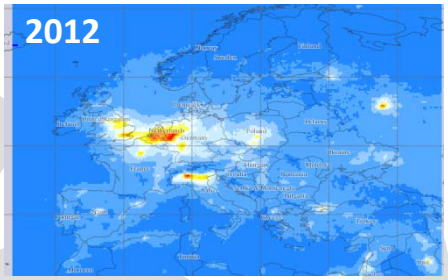



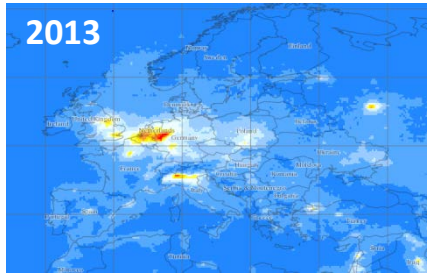



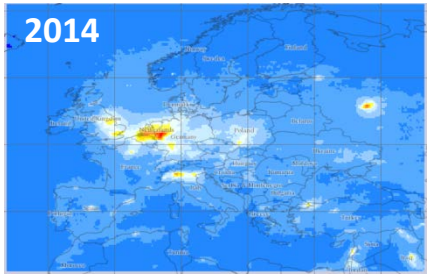



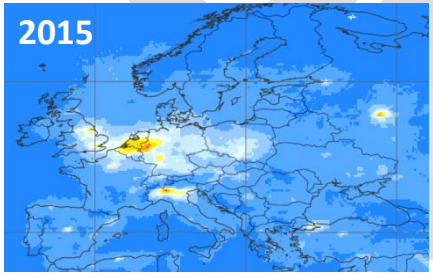



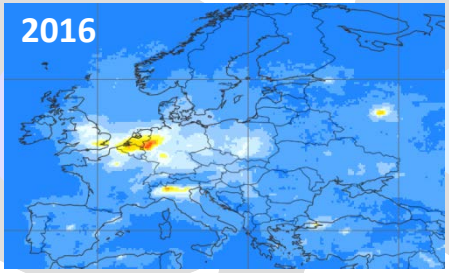



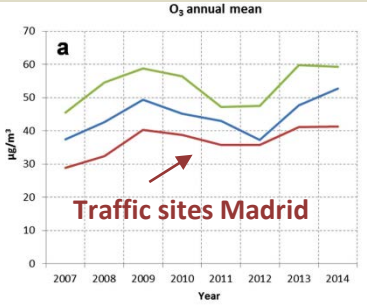



# Levels and time-trends of $O_3$ in Spain

**The issue of the origin of organic carbon in PM: Increasing oxidizing patterns**




$O_3$

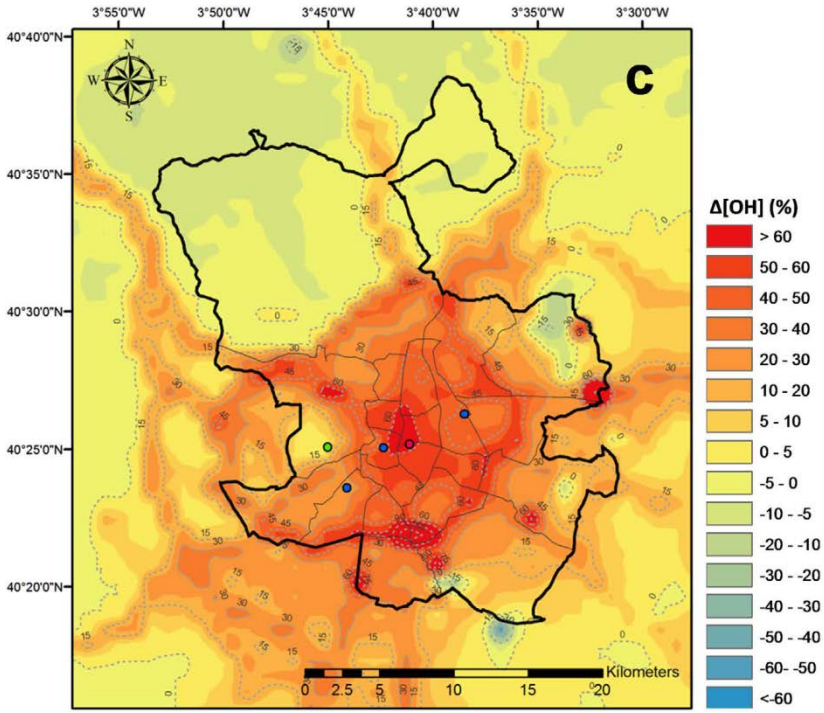
- Urban $O_3$ levels are increasing in many urban areas of the EU
- Causes:
  - Urban NOx decreased very smoothly, but NO more steeply
  - Saturated areas in NOx and VOCs sensitive
- Net effect: increasing oxidizing capacity of the urban atmosphere: higher PM (nitrate and SOA)

***Madrid city: Modelled 2004-2007 averaged annual increase in %***

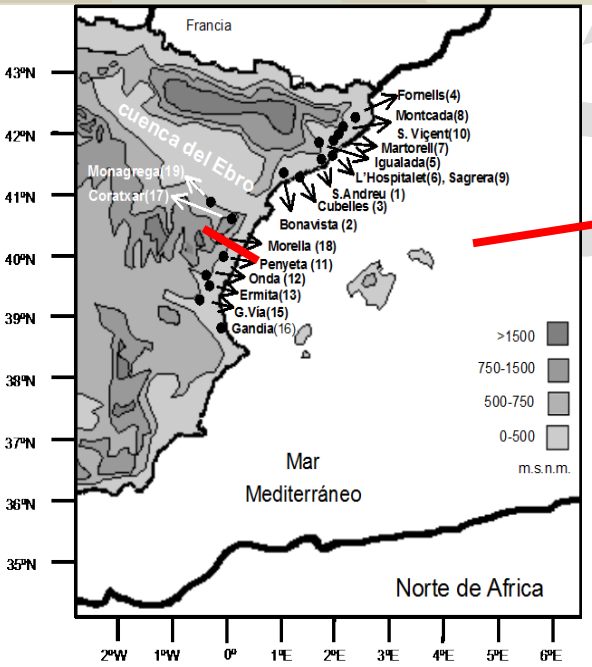
Saíz-López A. et al. (2017) Scientific Reports 7, 45956

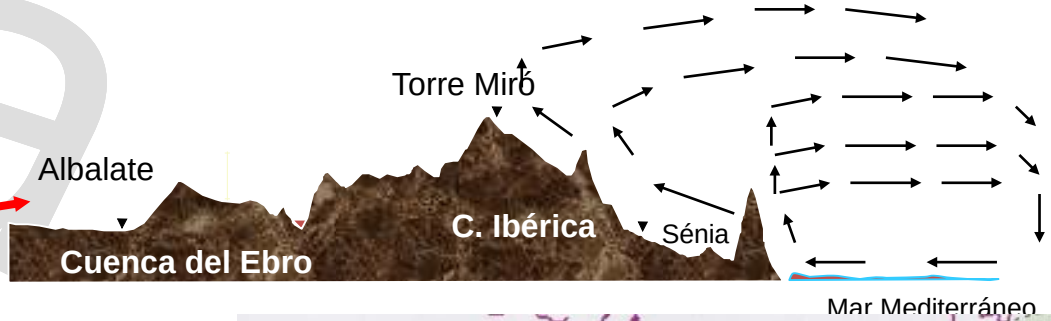
*OH radical*

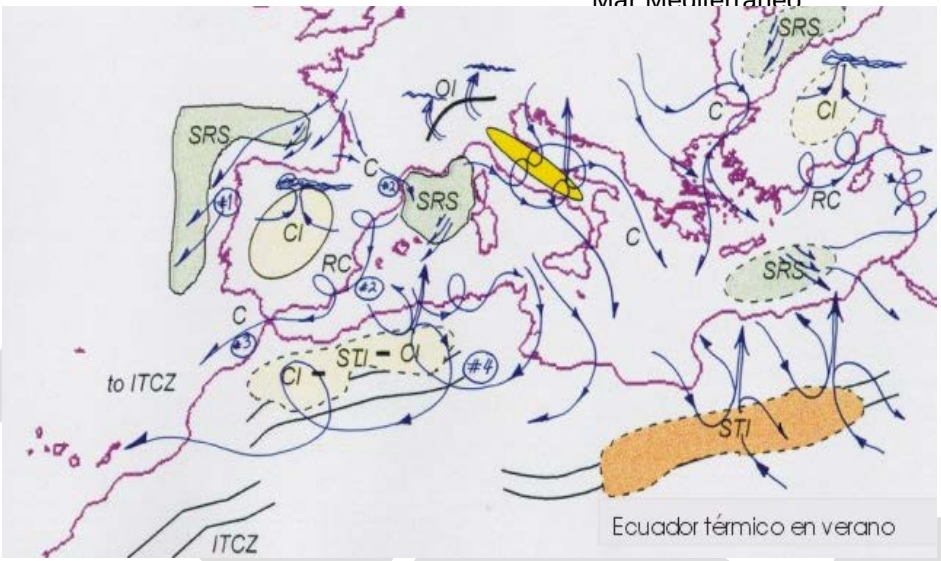
*$NO_3$ radical*

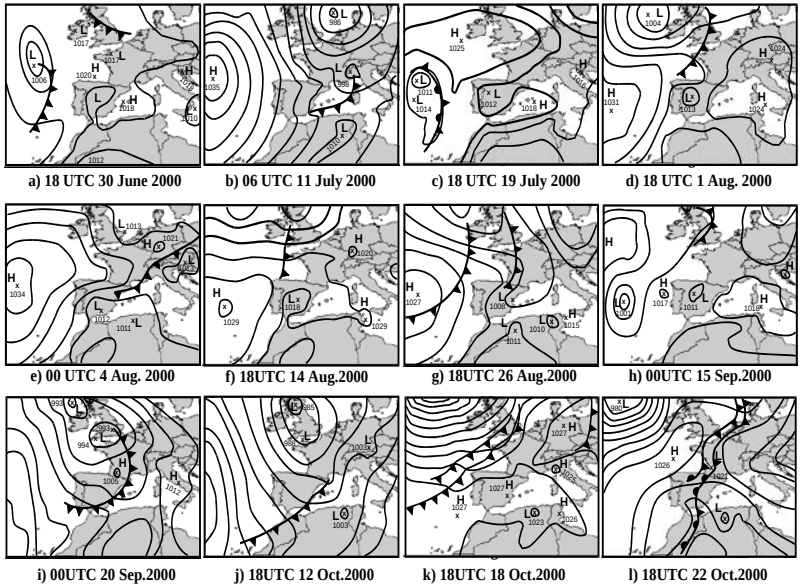


# Origin of $O_3$ in Spain



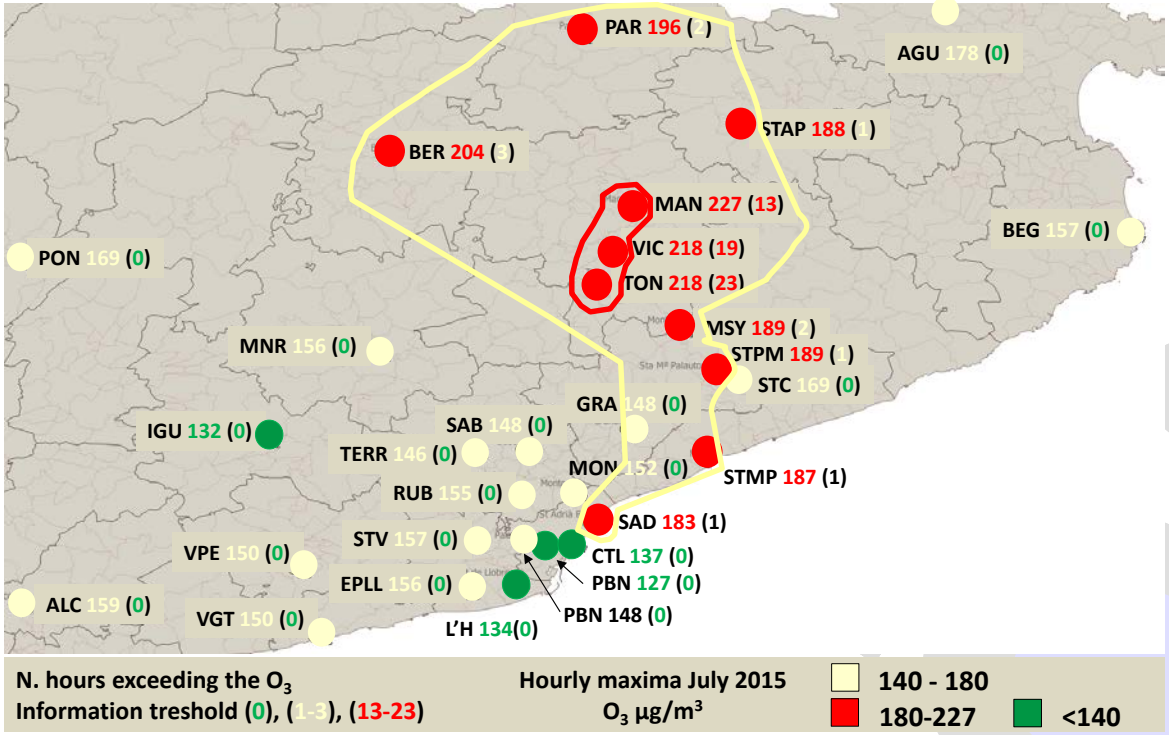




Millán et al., 1991, 1996a, 1996b, 1996c, 2000, 2002, 2014; Millán, 2002a; Millán and Sanz, 1999; Mantilla et al., 1997; Salvador et al., 1997, 1999; Gangoiti et al., 2001; Stein et al., 2004, 2005; Castell et al., 2008a, 2008b, 2012; Dieguez et al., 2009, 2014, Plaza et al., 1997

# Origin of $O_3$ in Spain

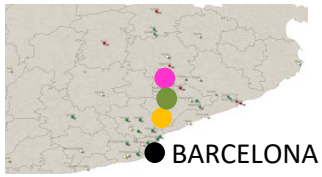
## Case study 1: N of Barcelona-Vic

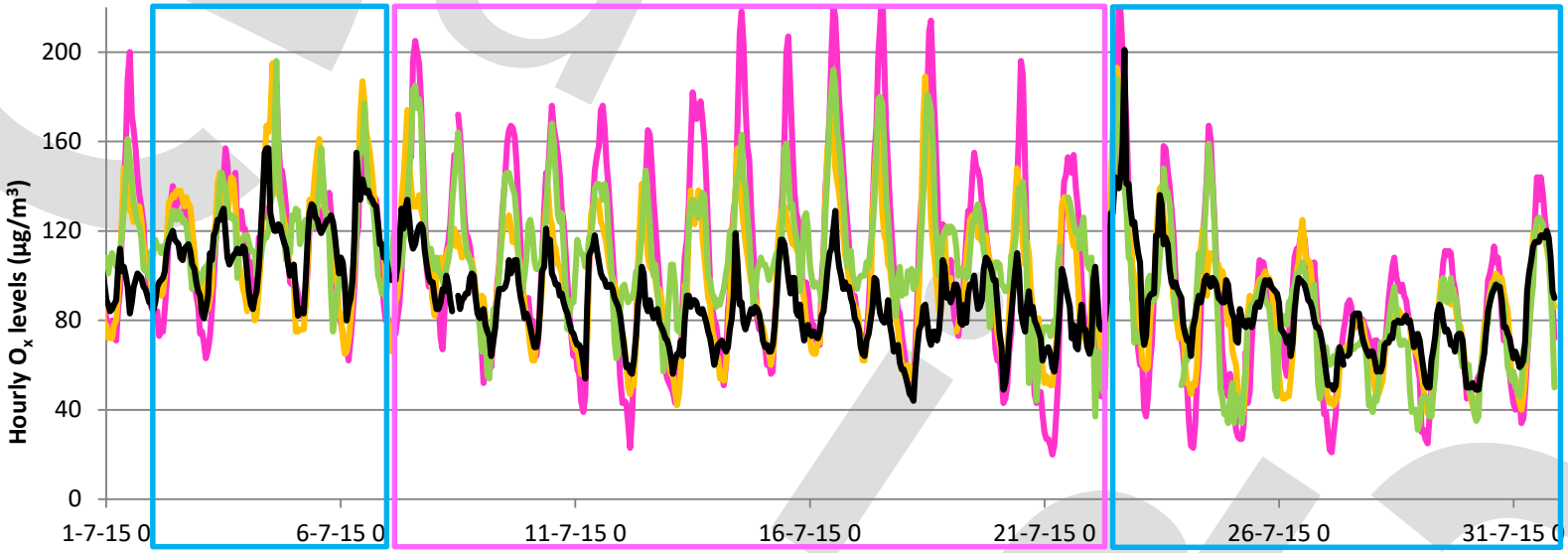
### Max-h (N. h >180 µg/m$^3$ $O_3$) July 2015



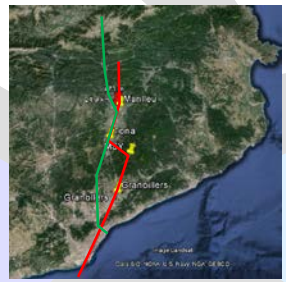
# Origin of $O_3$ in Spain

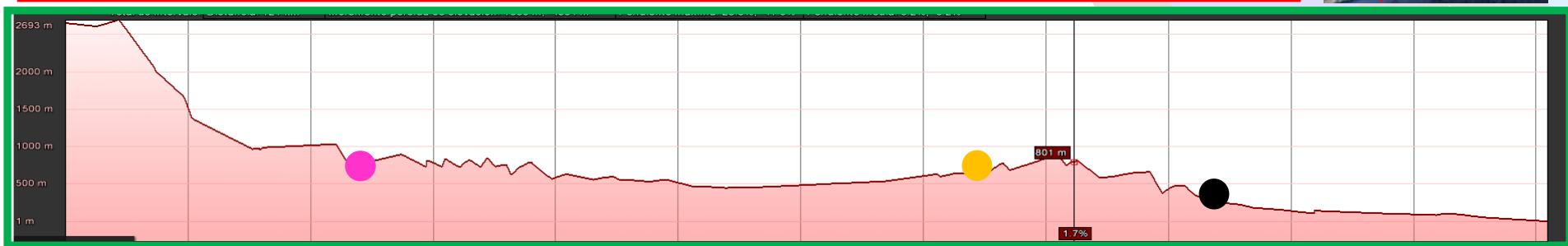
## Case study 1: N of Barcelona-Vic
## h-$O_x$=$NO_2$+$O_3$



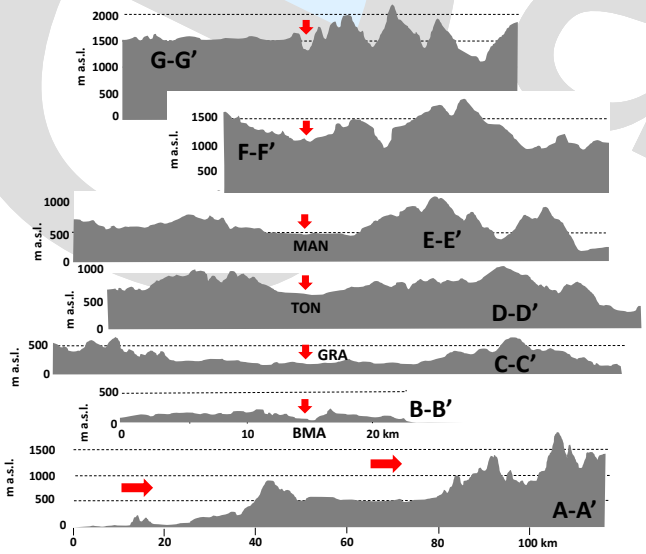




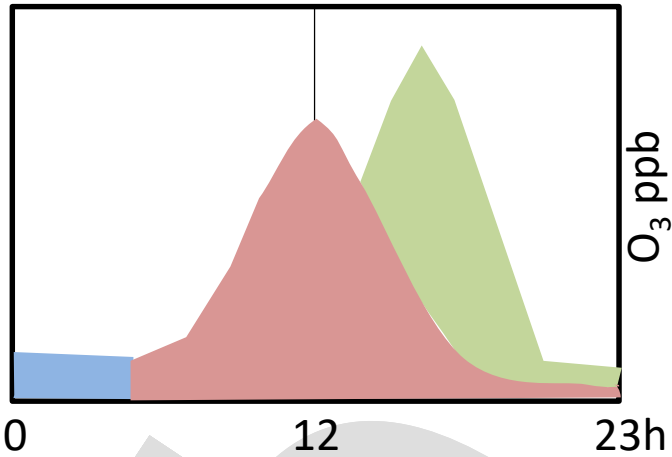


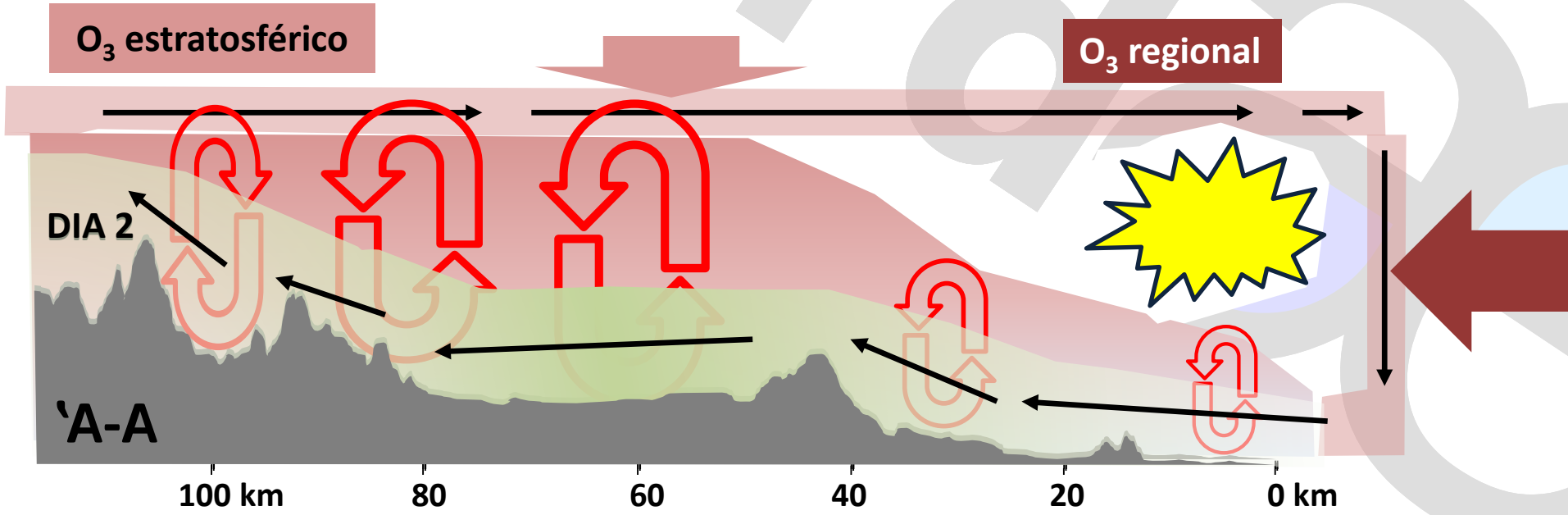
# Origin of $O_3$ in Spain

## Case study 1: N of Barcelona-Vic



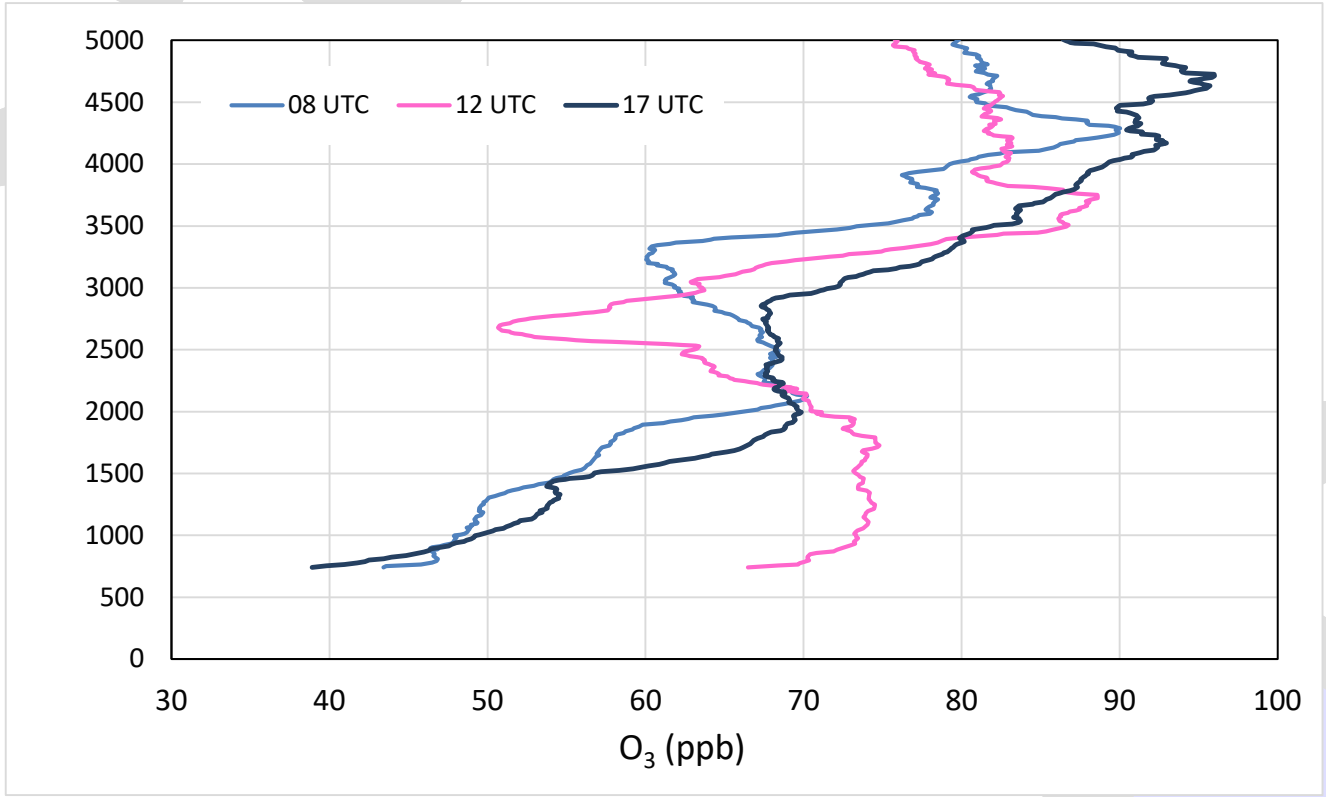




# Origin of $O_3$ in Spain

## Case study 1: N of Barcelona-Vic

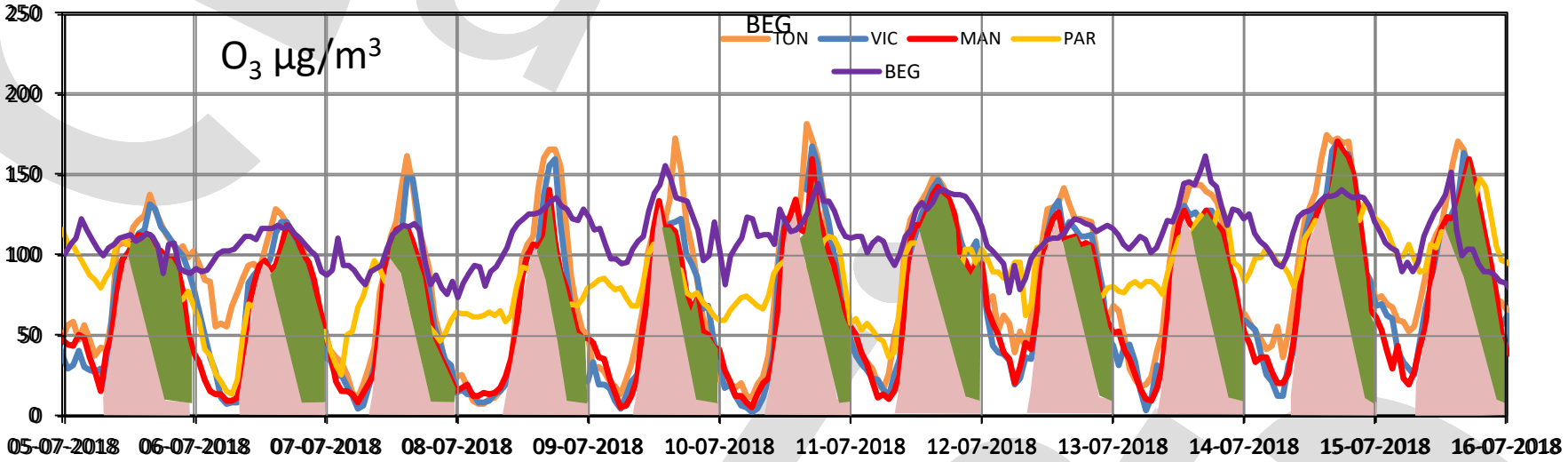



Montseny 13/07/2018

Fuente: Colaboración AEMET-IDAEA(CSIC)

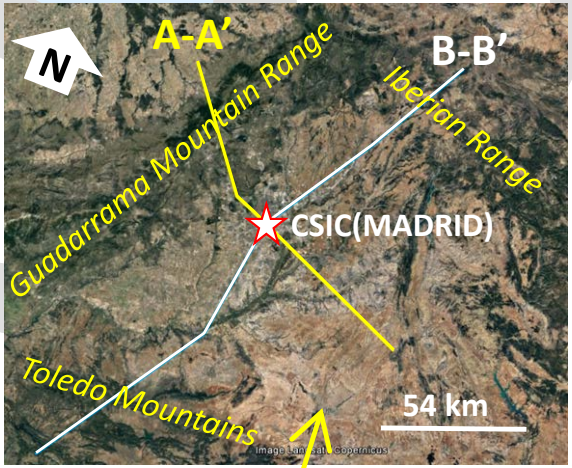
# Origin of $O_3$ in Spain

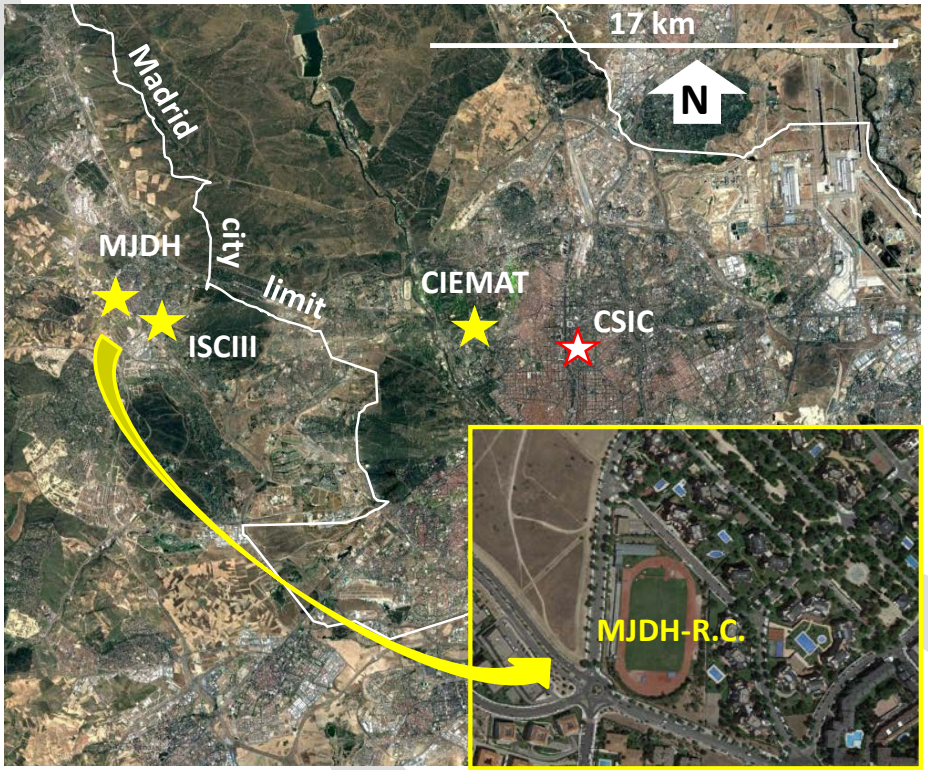
## Case study 1: N of Barcelona-Vic

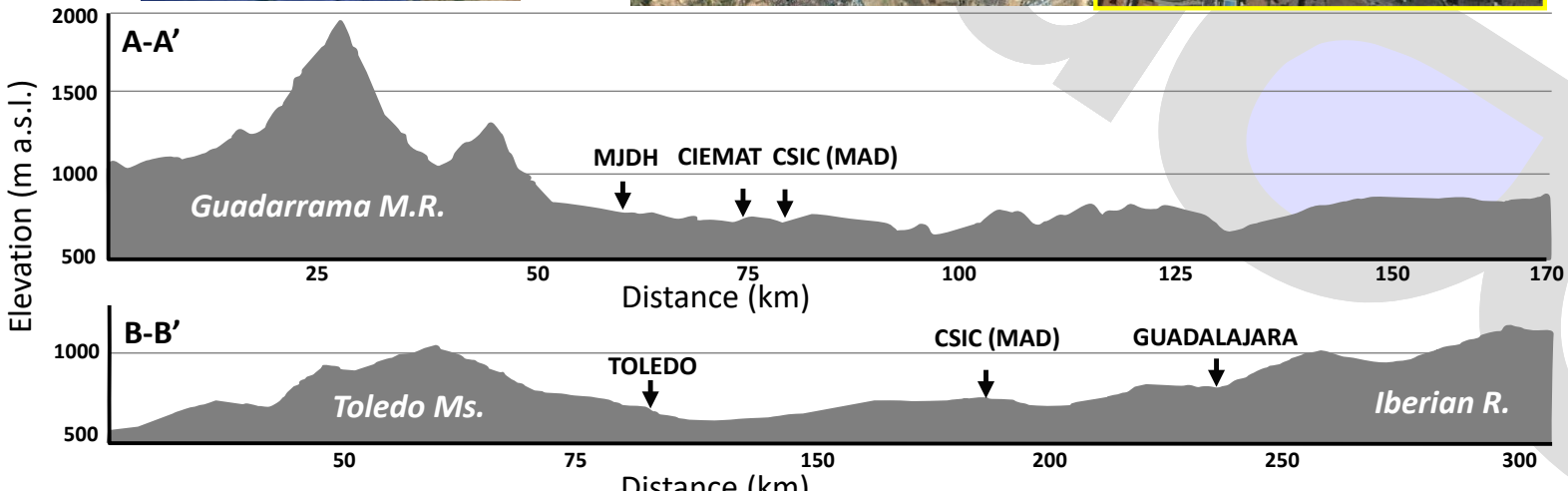


# Origin of $O_3$ in Spain

## Case study 2: Madrid

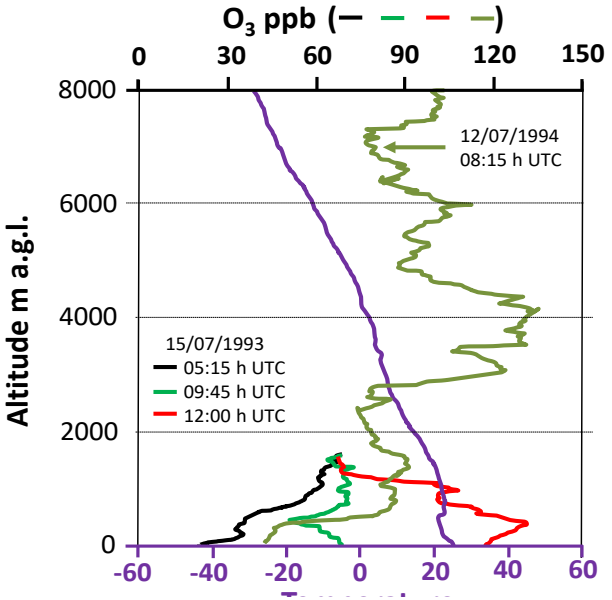


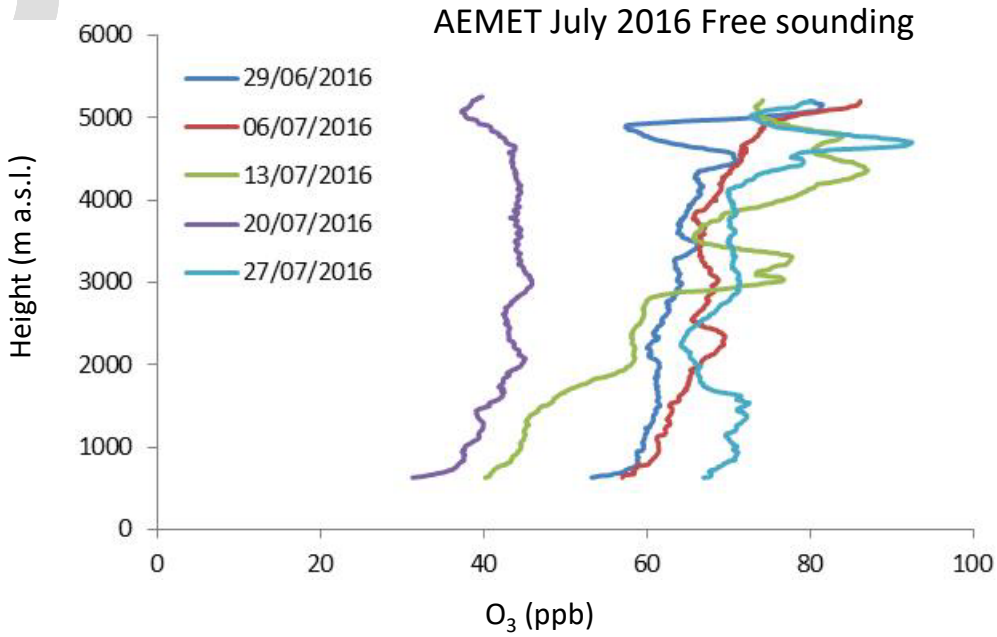



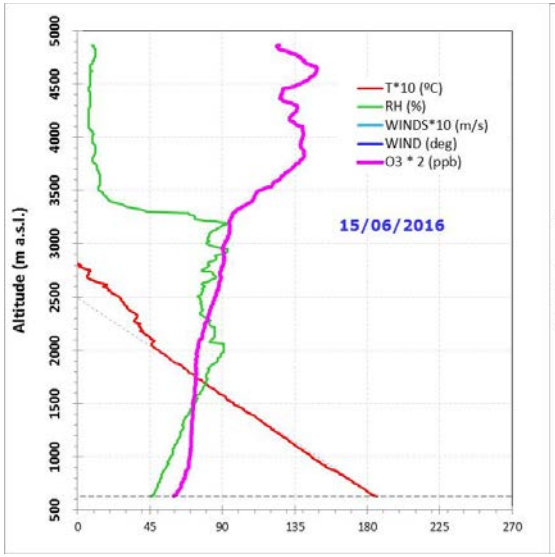
# Origin of $O_3$ in Spain

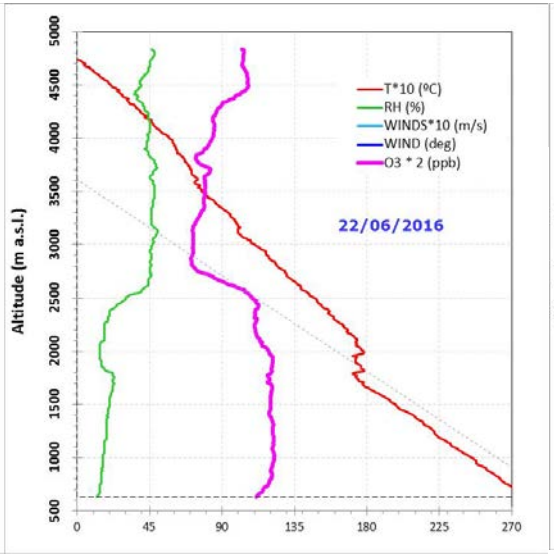
## Case study 2: Madrid

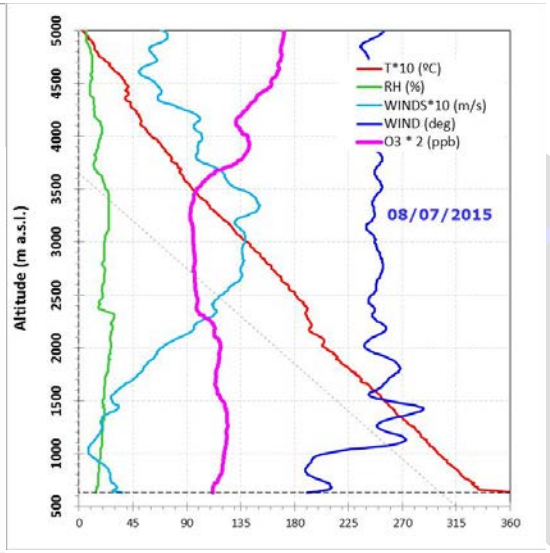



Plaza et al., 1997



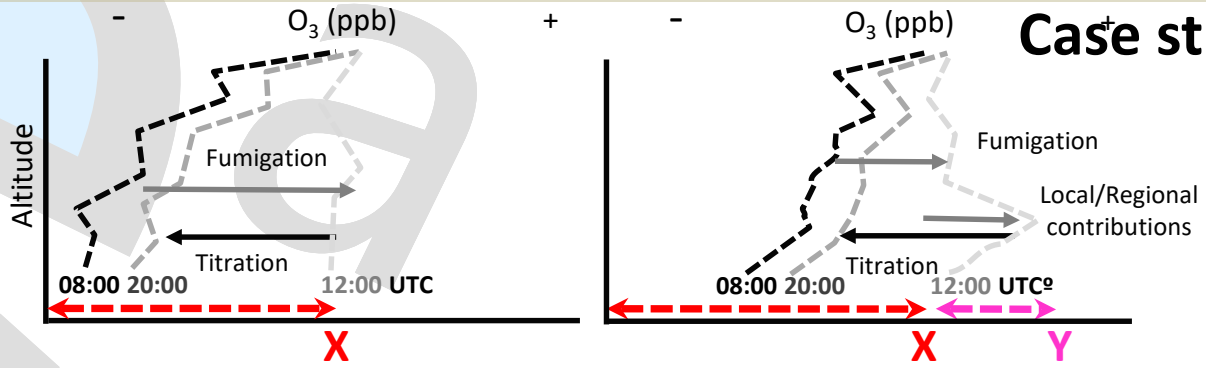



# Origin of $O_3$ in Spain

## Case study 2: Madrid

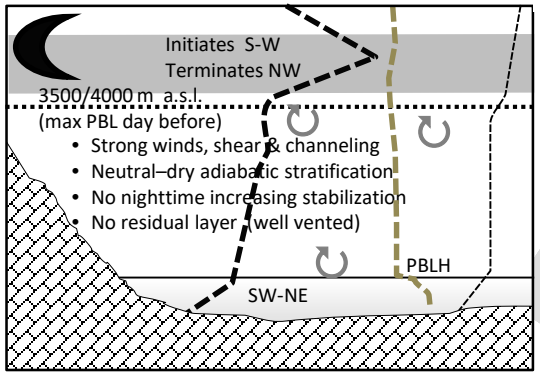



### VENTING/TROUGHING (VT EVENT)

Free troposphere. Strong winds
Occasional high $O_3$ strata (regional-external, free-troposphere $O_3$)

**Low $O_3$ (mixed, more external)**
**Intense ventilation,** no accumulation from the day before
Mechanical Turbulence

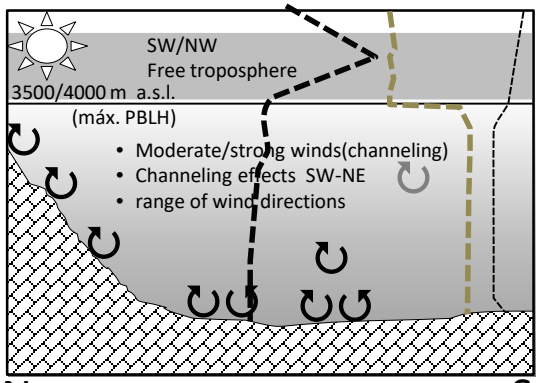
Surface layer, occasionally stably stratified
**Low $O_3$ concentrations, titration**
Strong winds SW-NE




Strong winds

**No $O_3$ accumulation in the PBL**
No re-circulatory winds
**New $O_3$ /UFP formation**
**$O_3$ fumigation**

Thicker PBL: > 2000-2500 m a.s.l. at 12:00 UTC
Rapid growing up to 3500/4000 m
Intense mechanical & convective turbulence; Intense convection

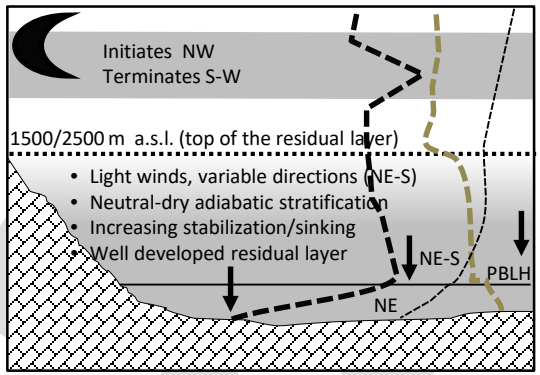



### ACCUMULATING/RIDGING (AR EVENT)

Free troposphere. Light winds
Occasional high $O_3$ peaks (regional-external, free-troposphere $O_3$)

**Higher $O_3$ (mixed external + Local)**
**Low ventilation**, re-circulatory winds, accumulation from the day before
No Turbulence

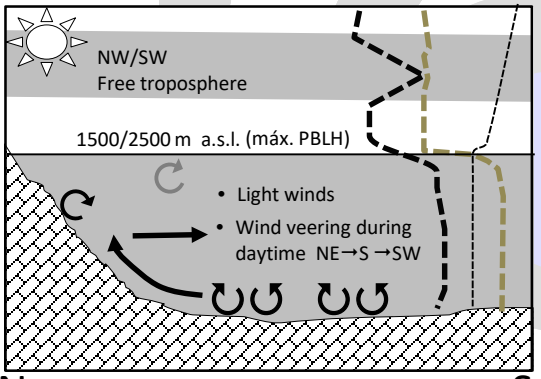
NE'ly jet over stably stratified surface layer
**Low $O_3$ concentrations, titration**
Light winds (NE).




Light winds

**$O_3$ accumulation in the PBL**
Re-circulation over the MMA basin
**New ozone/UFP formation, $O_3$ fumigation**

Thinner PBL: < 1500 m a.s.l. at 12:00 UTC
Slower deepening to 1500/2500 m
Intense convective turbulence
**Additional $O_3$ formation of local origin**
Thermally driven wind veering NE→S →SW
Intense convection



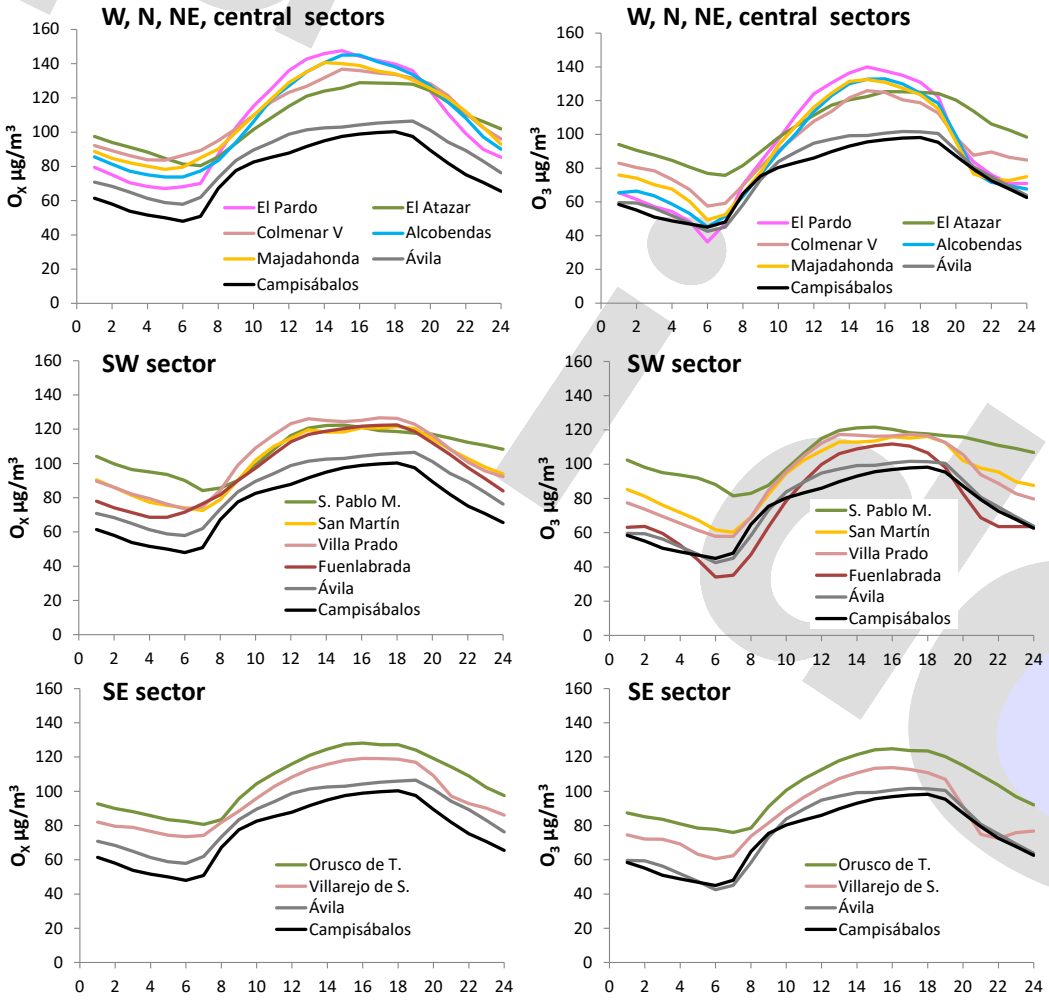

$O_3$ | UFP | Potential T | Height PBL | High altitude $O_3$ strata

Convection | Turbulence | Sinking | Thermally driven circulations

# Origin of $O_3$ in Spain

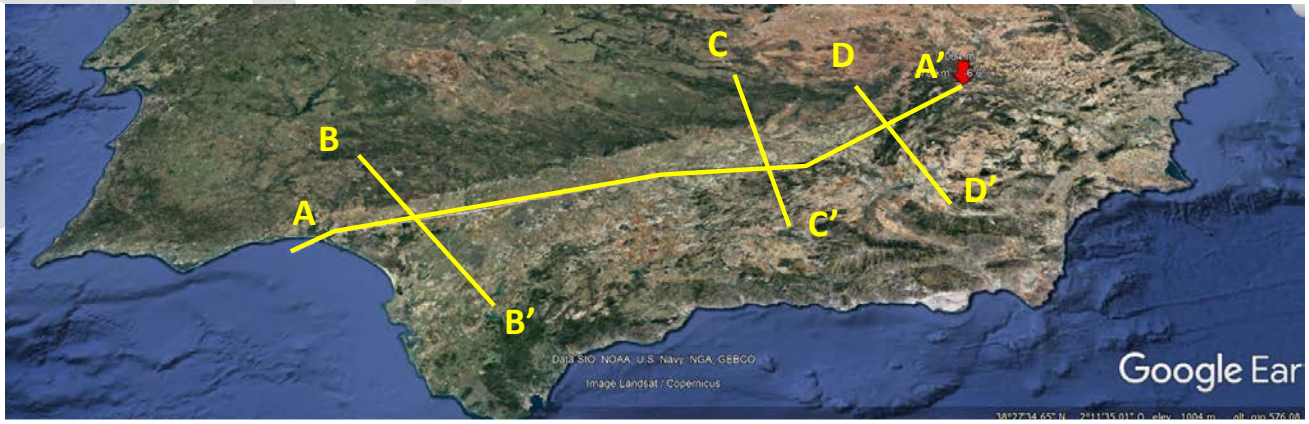
## Case study 2: Madrid

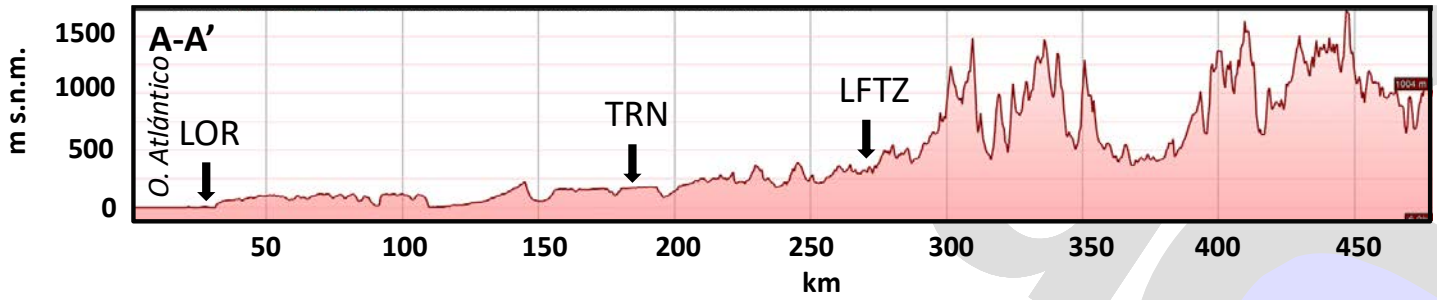
JULY 2016

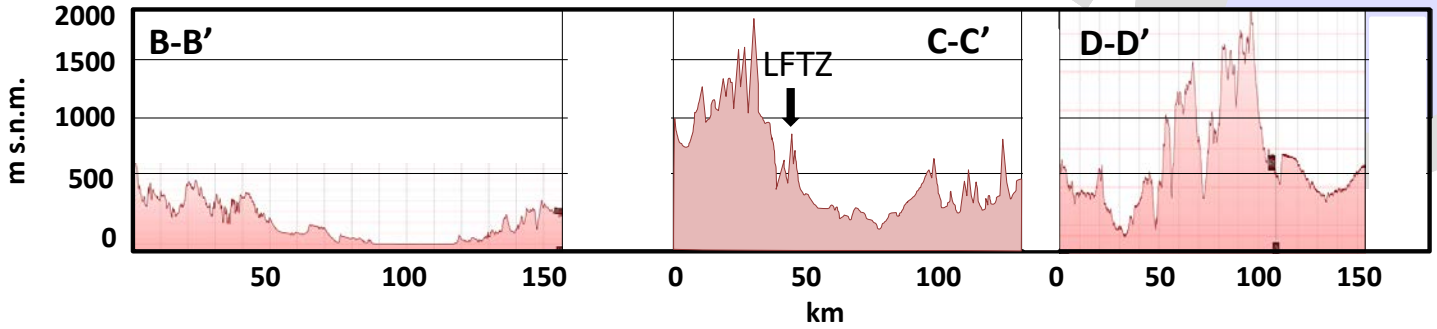


# Origin of $O_3$ in Spain

## Case study 3: Guadalquivir Valley



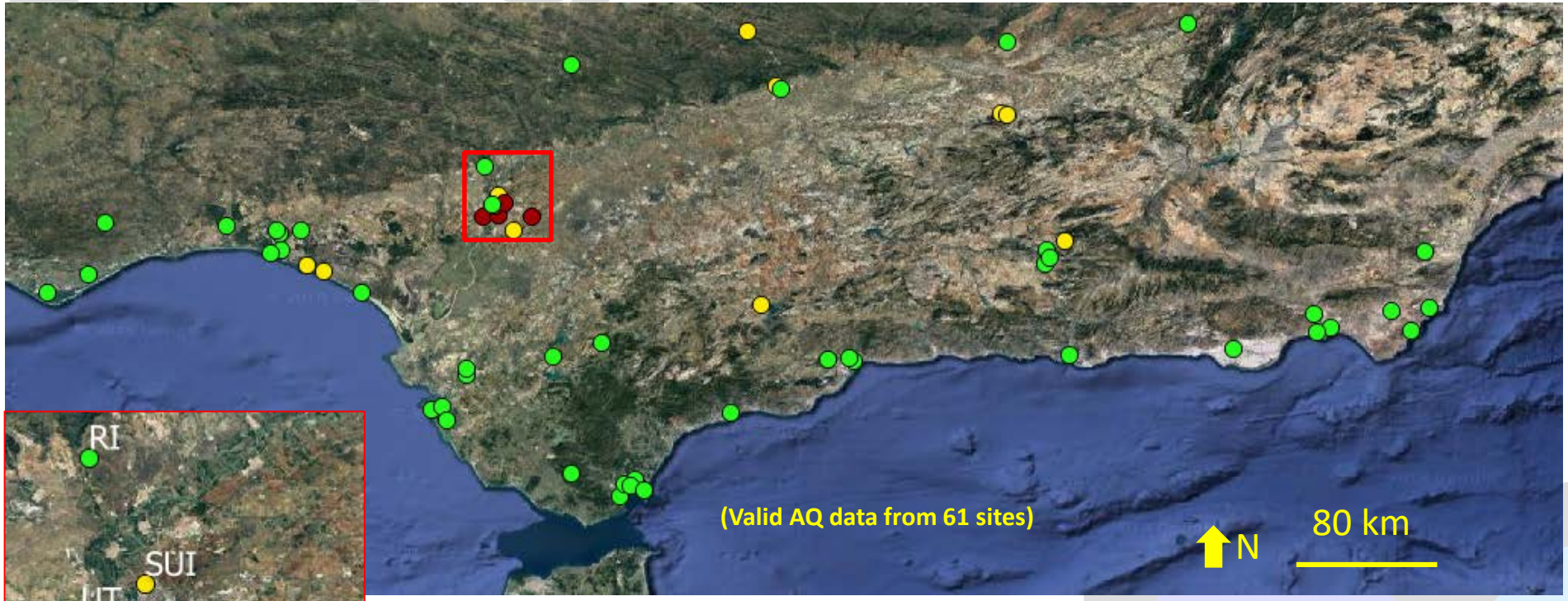



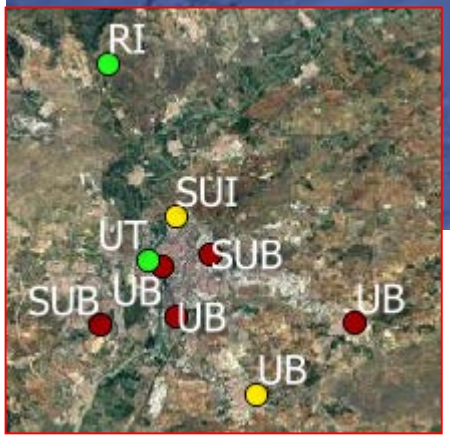
# Origin of $O_3$ in Spain

## Case study 3: Guadalquivir Valley

Average number of h exceedances > 150 µg $m^{-3}$ $O_3$ per site per year 2005-2018

Years with minimum of 75% APR-SEP hourly data availability. Minimum of 7 years of valid data within 2005-2018




Sevilla

#avg. h exceed./site · year

- 0 - 13 [46]
- 13 - 25 [10]
- 25 - 38 [5]

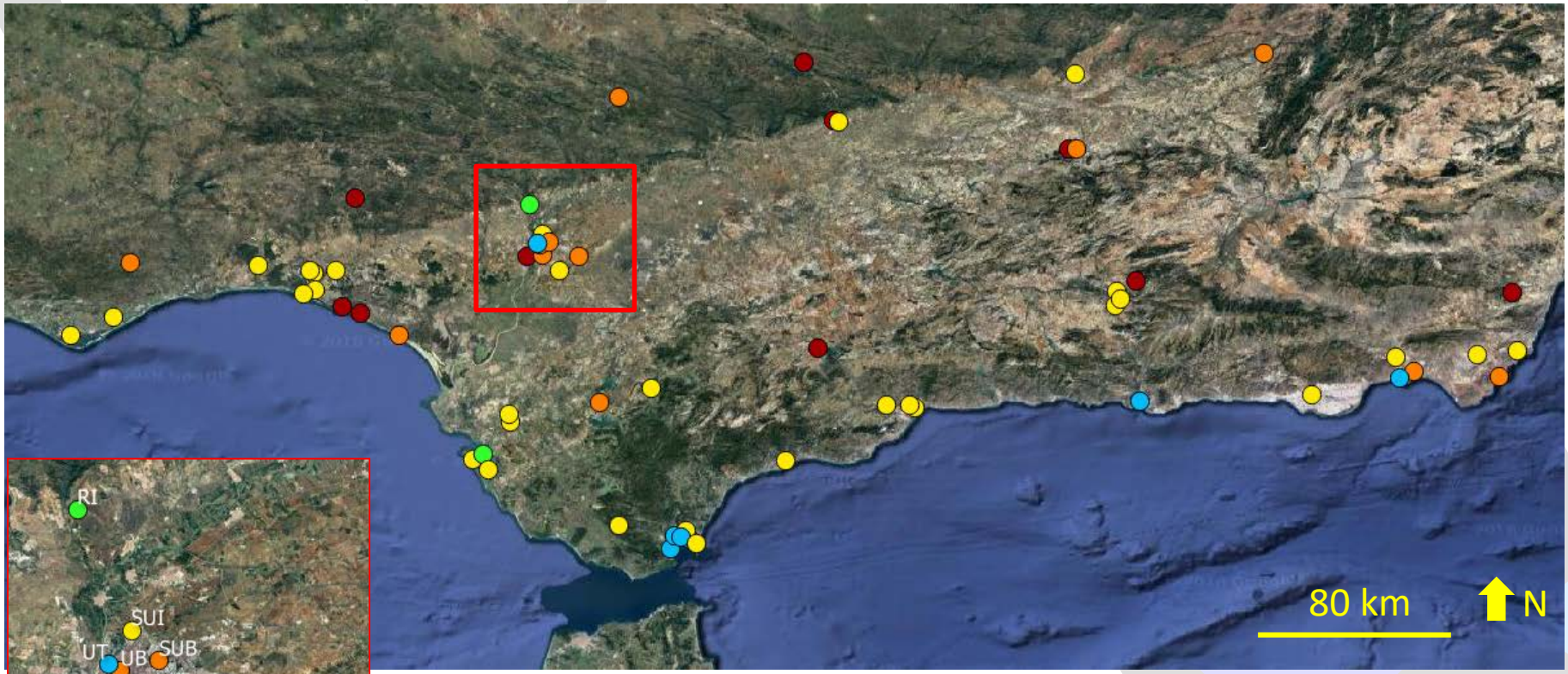
>150 µg $m^{-3}$ $O_3$

# Origin of $O_3$ in Spain

## Case study 3: Guadalquivir Valley

Average percentile 93.2 $O_3$ 2005-2017

Minimum 6 years of valid data: (minimum of 75% APR-SEP of $O_3$ hourly data availability)




Sevilla

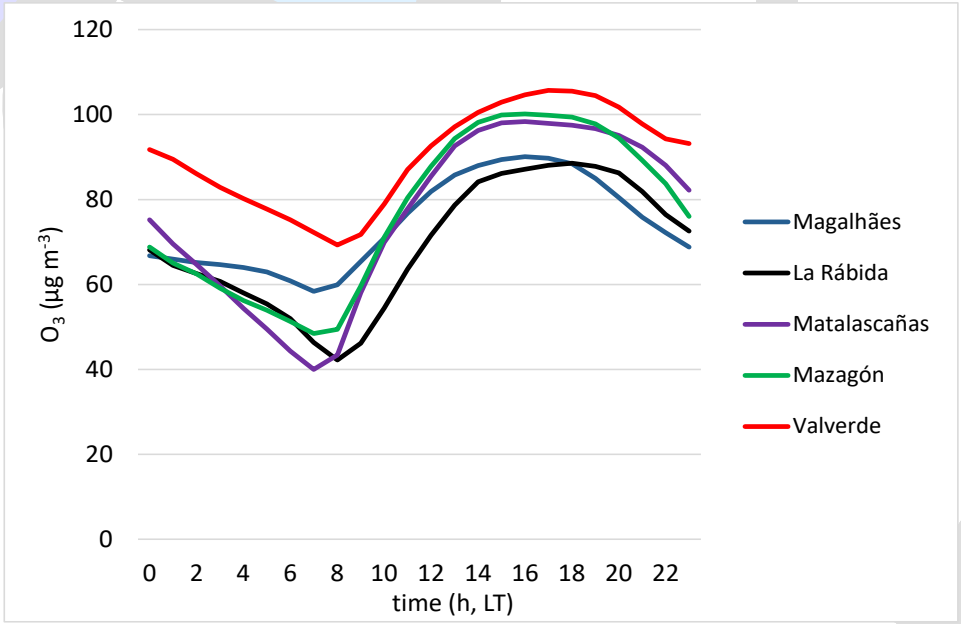
(Valid AQ data from 62 sites)

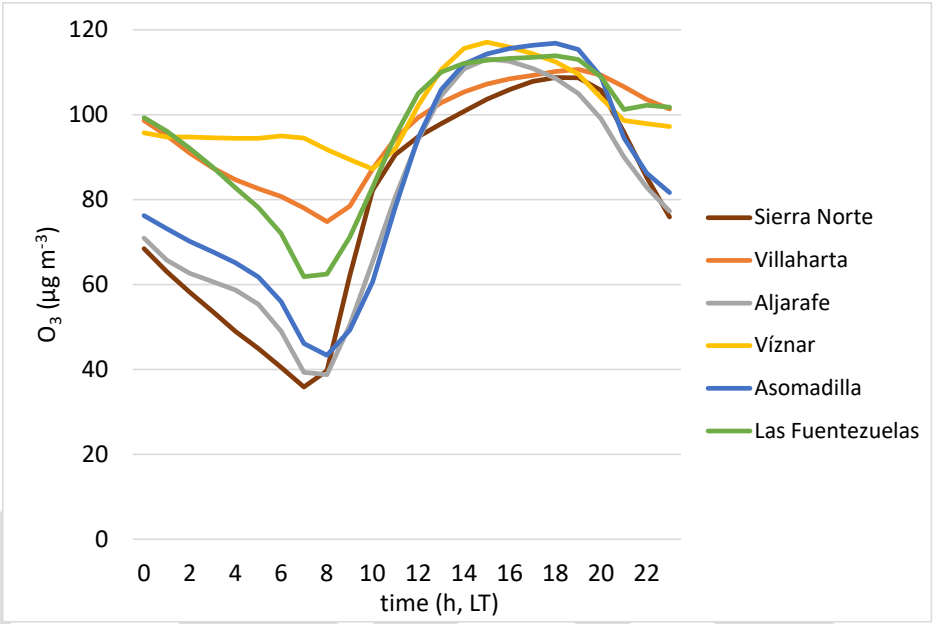
96 - 104 [7]
104 - 110 [2]
110 - 120 [31]
120 - 125 [12]
125 - 130 [10]

Avg. P93.2 $O_3$ (µg $m^{-3}$)

# Origin of $O_3$ in Spain

## Case study 3: Guadalquivir Valley




# Implications for air quality management

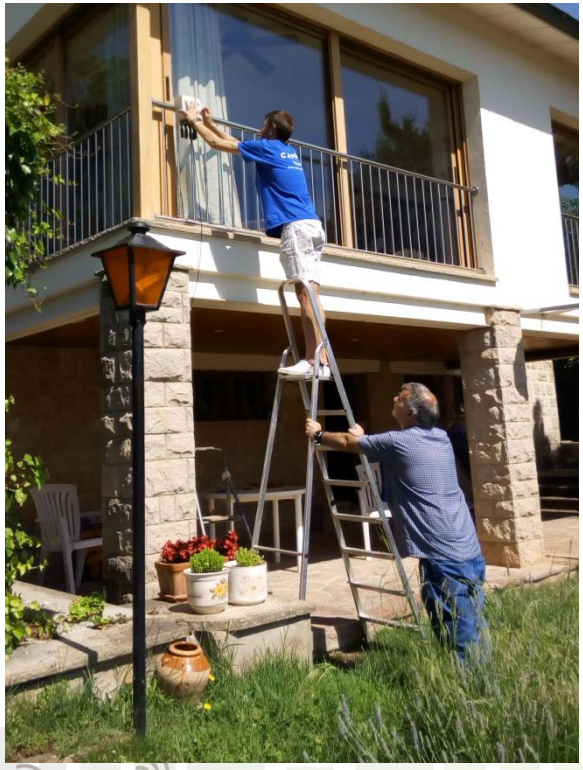
- The $O_3$ problem is one of the most complex in air quality; solutions are therefore complex as well
- We suggest implement measures for the most acute episodes in parallel with the structural actions to reduce everyday $O_3$
- Exceedances of 180µg / $m^3$ h-$O_3$ are recorded in 7 specific areas of Spain and have overlying local, regional and long distance contributions (Diéguez et al., 2014, Querol et al., 2016). Policies are needed at all 3 scales, BUT THE LOCAL/REGIONAL ONE IS VERY IMPORTANT during the most acute episodes
- The relative origins of $O_3$ (hemispheric, regional, local) vary in proportion in the different basins areas of Spain
- To reduce $O_3$ it is necessary to abate precursors structurally (May-August), rather than episodic
- Episodic measures can be effective for the most acute episodes if:
  - Meteorological forecast of recirculation episodes and mixing layer depth (Millán et al., 1997 and 2000) are carried out
  - Sensitivity studies for reductions of VOCs and $NO_X$
- Peak episodes decreased in the last decade and urban $O_3$ is growing and the impact on increase of radicals (and PM2.5 and OVOCs ) is demonstrated already

# Citizen Awareness on Tropospheric $O_3$ Pollution : CAPTOR

CAPTOR
COLLECTIVE AWARENESS PLATFORM
FOR TROPOSPHERIC OZONE POLLUTION

European Commission

## Monitoring $O_3$ in volunteers' homes



2016 2017 2018

# Online $O_3$ data

CAPTOR AIR

Map | List of stations | Station | About

EN | ES | CA | DE | IT

https://captorair.org/list/


Good Moderate Poor Very poor

Sant Vicenç de Torelló

Ozone hourly mean — 50 ug/m3

25/07/2017 07:30:02 UTC

Ozone eight hours mean — 33 ug/m3

25/07/2017 07:30:02 UTC

The data generated by the CAPTOR nodes should only be considered informative and not be used for regulatory compliance purposes.

# Acknowledgements

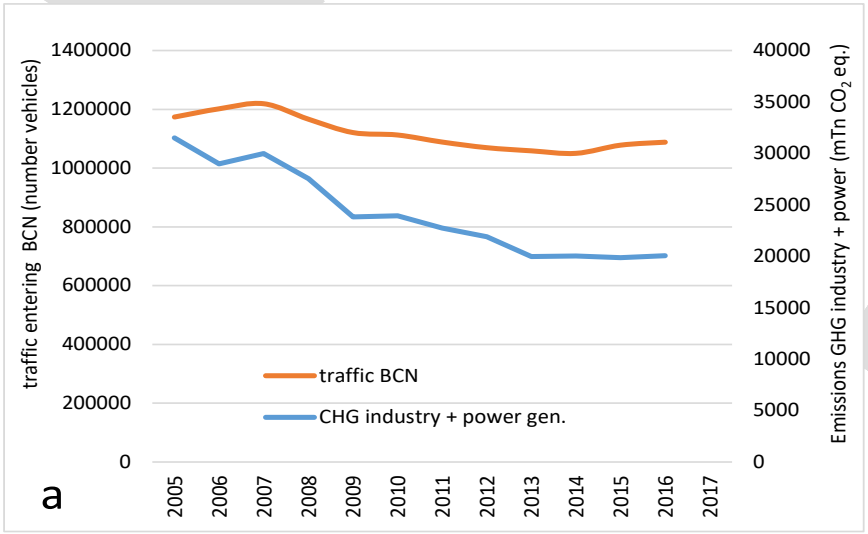
house.

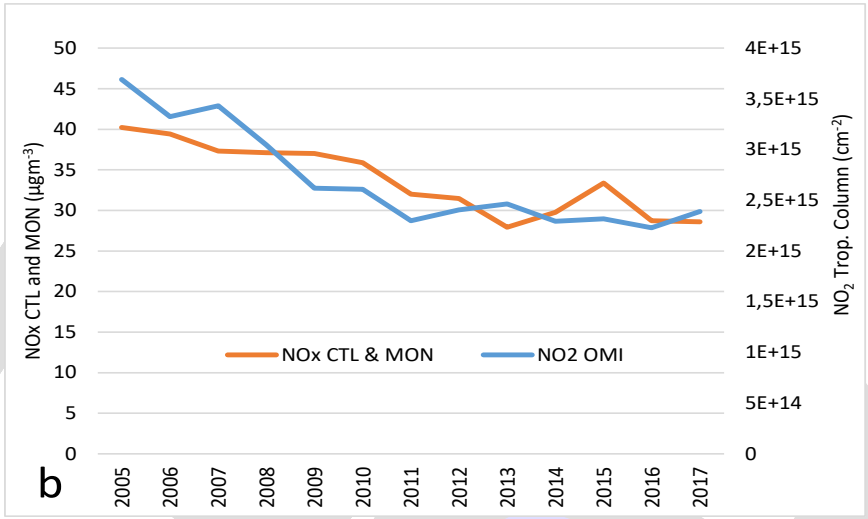
HIGH OZONE, ULTRAFINE PARTICLES AND SECONDARY ORGANIC AEROSOLS
CGL2016-78594-R

**Thank you very much!!!!**

**Xavier.querol@idaea.csic.es**

# Levels and time-trends of $O_3$ in Spain

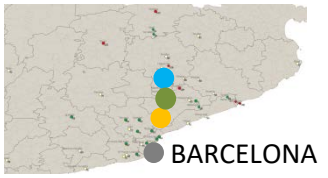


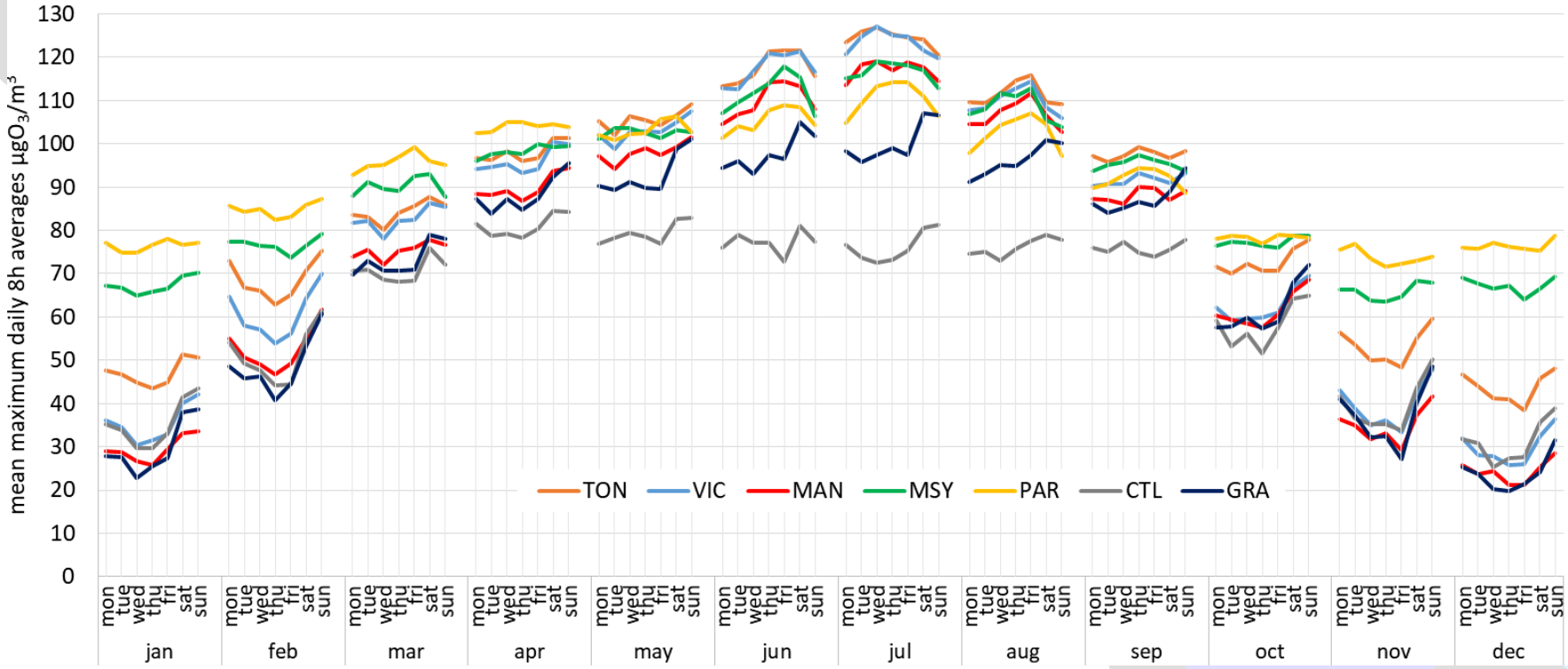




Tesis Final de Master Jordi Massagué, 2018 (Master Ingeniería Ambiental, UPC-IDAEA-CSIC)

# Origin of $O_3$ in Spain

## Case study 1: N of Barcelona-Vic




Tesis final de Master Jordi Massagué (Master Ingeniería Ambiental, UPC-IDAEA-CSIC)

# Levels and time-trends of $O_3$ in Spain

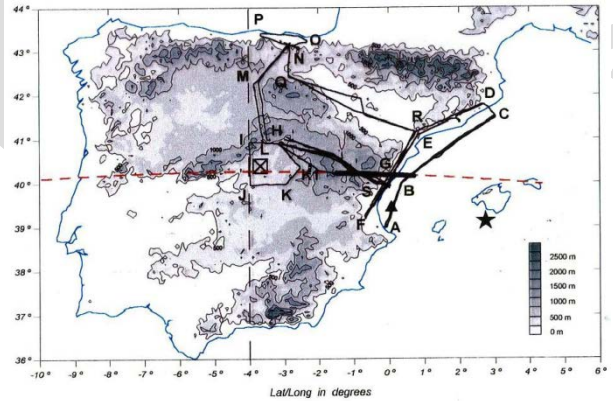
- Analysis of 2000-2015 $O_3$ data in Spain

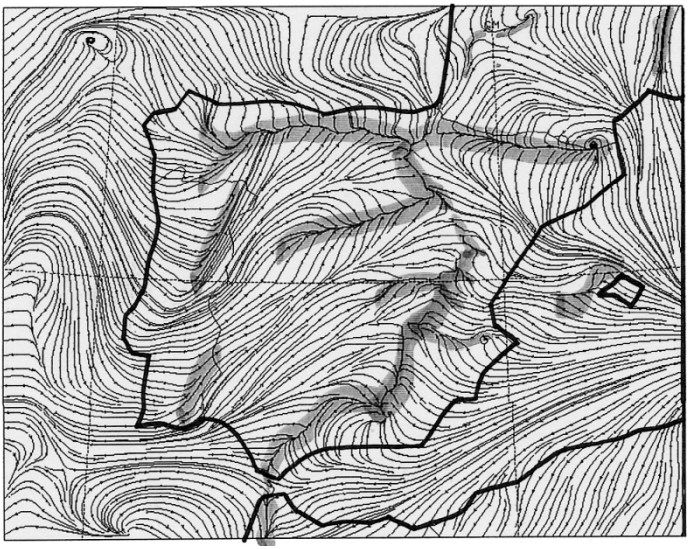

- 245 AQ monitoring sites
- Measuring 10/16 years
- With data for 2014-2015
- >85% data coverage in summer
- Used at least 1 year for official AQ reporting to the EC

QUEROL X., ALASTUEY A., RECHE C., ORIO A., PALLARES M., REINA F., DIEGUEZ JJ., MANTILLA E., ESCUDERO M., ALONSO L., GANGOITI G., MILLÁN M. On the origin of the highest ozone episodes in Spain. Science of the Total Environment 572 (2016) 379-389.

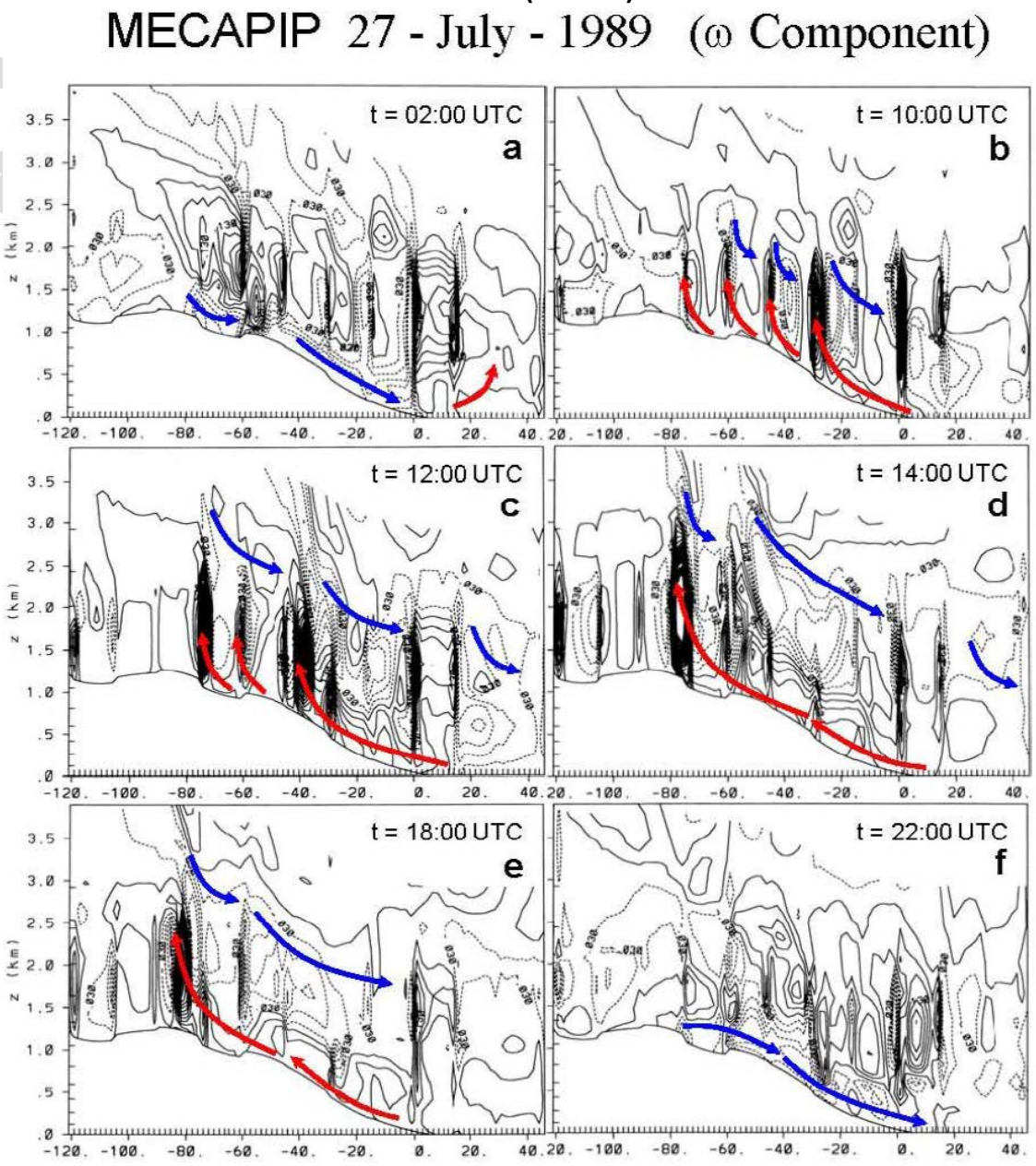
# Origin of $O_3$ in Spain

Millán et al (2002) Environ Poll.



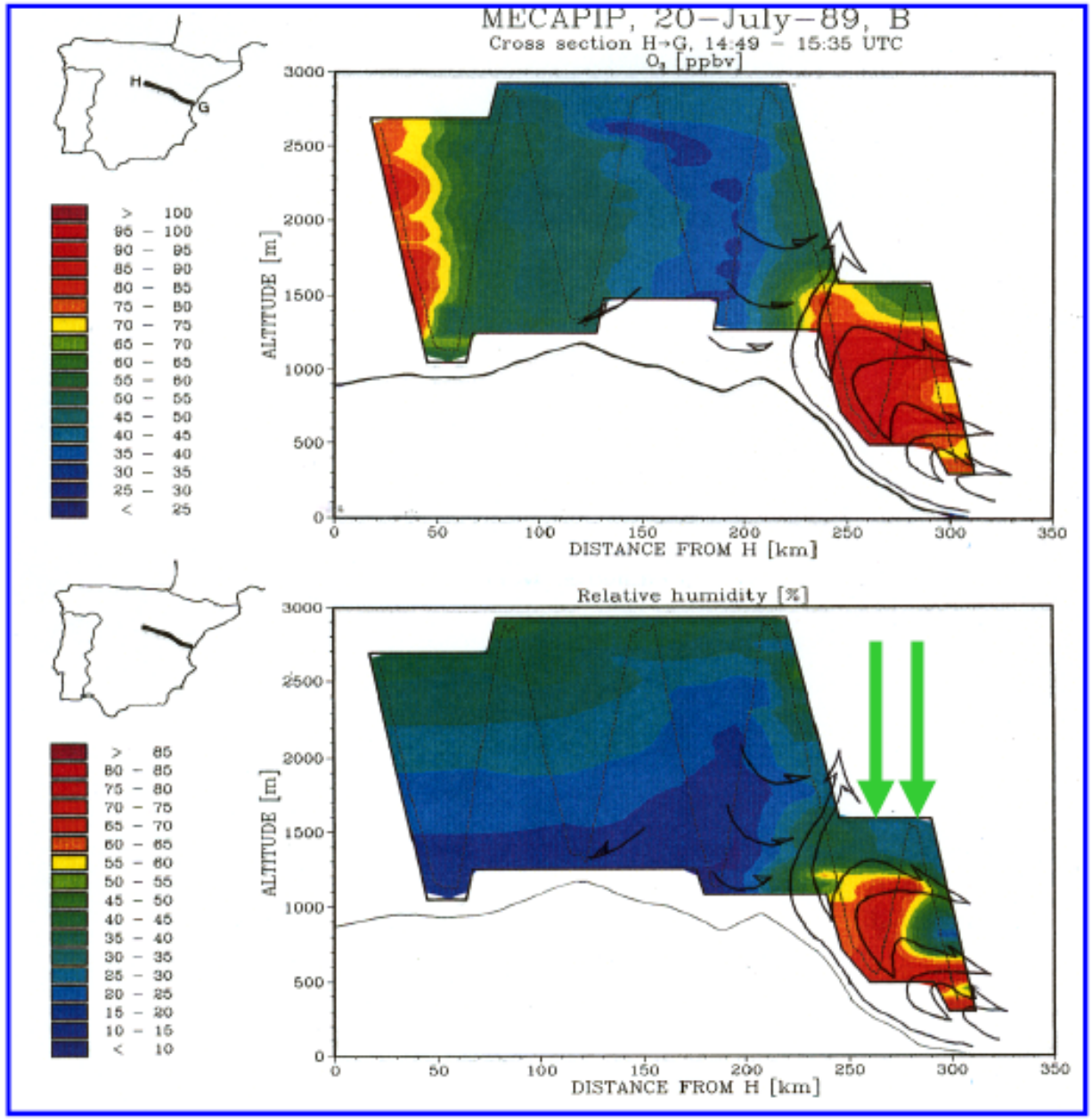



Salvador et al. (1997) Int. J. Env. Poll.




**Courtesy M. Millán, CEAM**

# Origin of $O_3$ in Spain

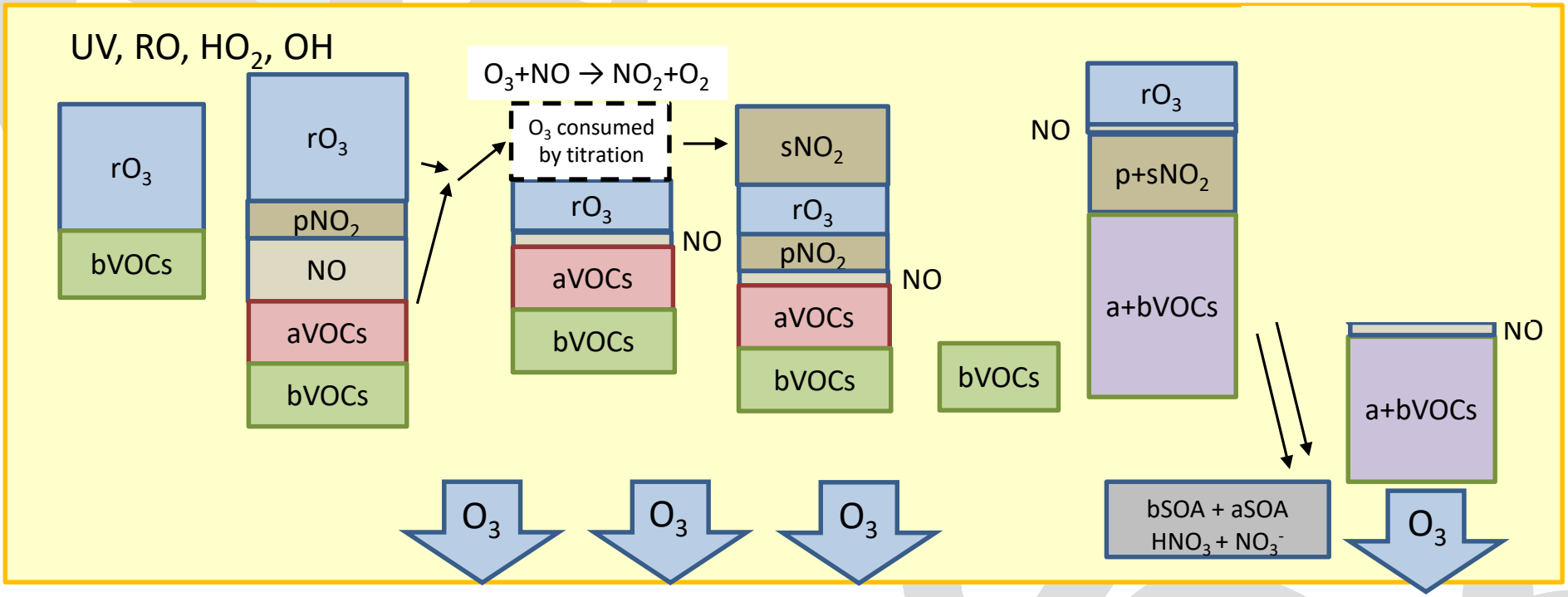



**Courtesy**
**M. Millán, CEAM**

**Millán et al (1996)**
**Atmos Environ**

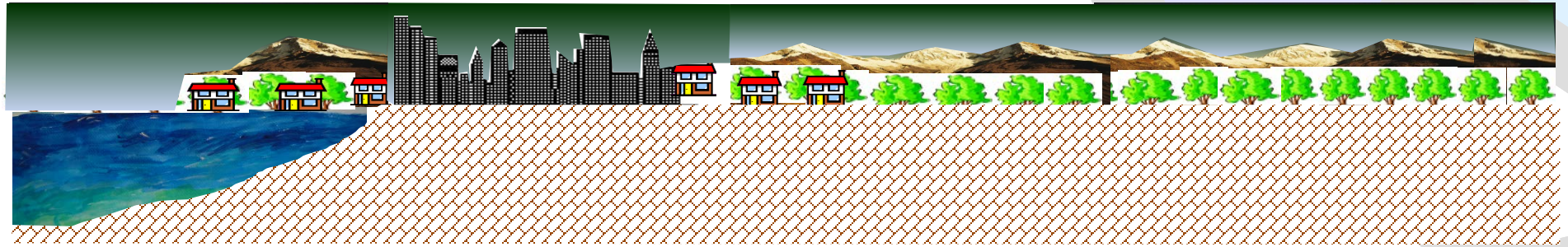
# Origin of $O_3$ in Spain

## The complex atmospheric circulations driving $O_3$ episodes in the Mediterranean



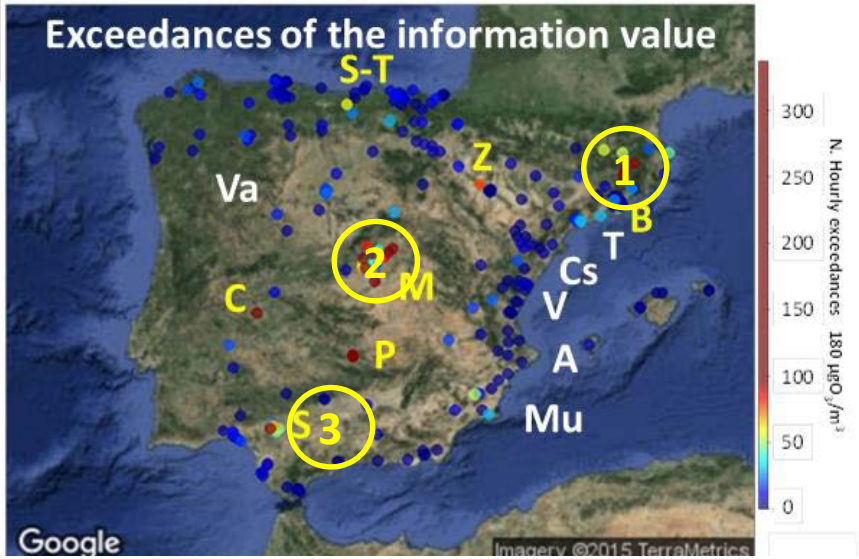

Ozone dry deposition (Monks et al., 2015):

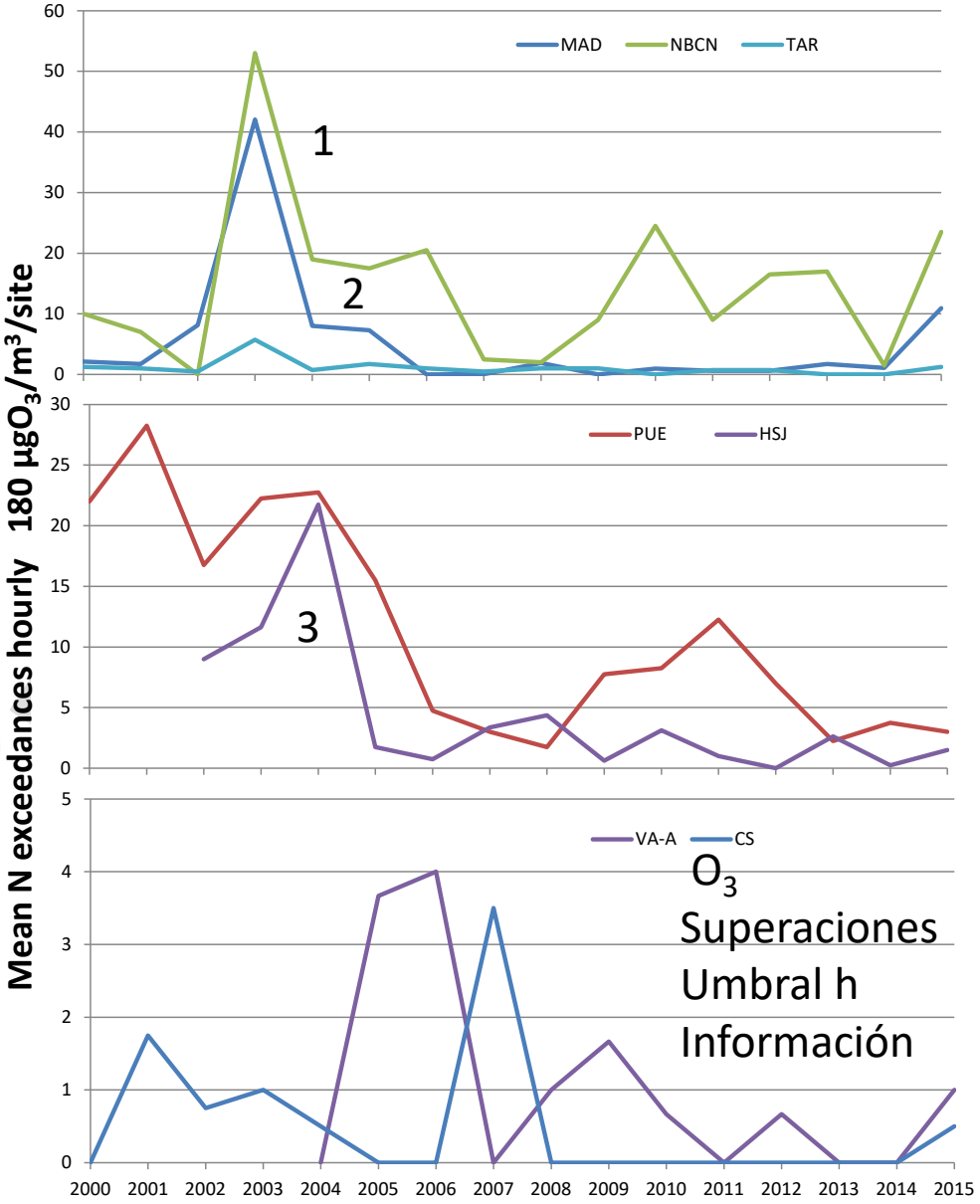
- -Stomatal deposition
- -Non stomatal depostion
- -Radiation & surface-T reactions
- -In-canopy chemistry (NO)
- -Deposition to Water



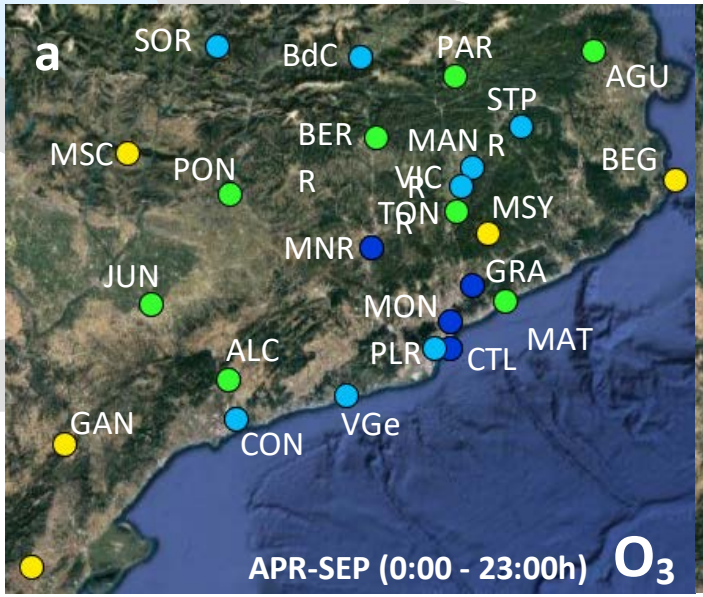
# Origin of $O_3$ in Spain

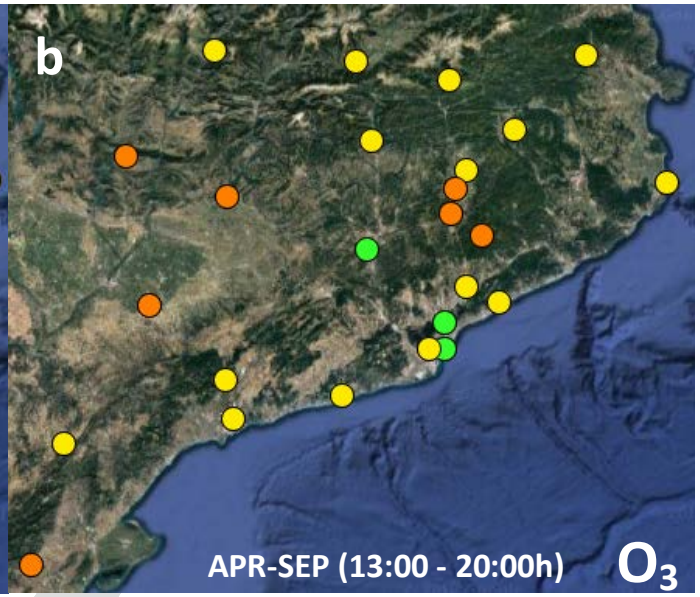
## $O_3$ episodes in three atmospheric basins



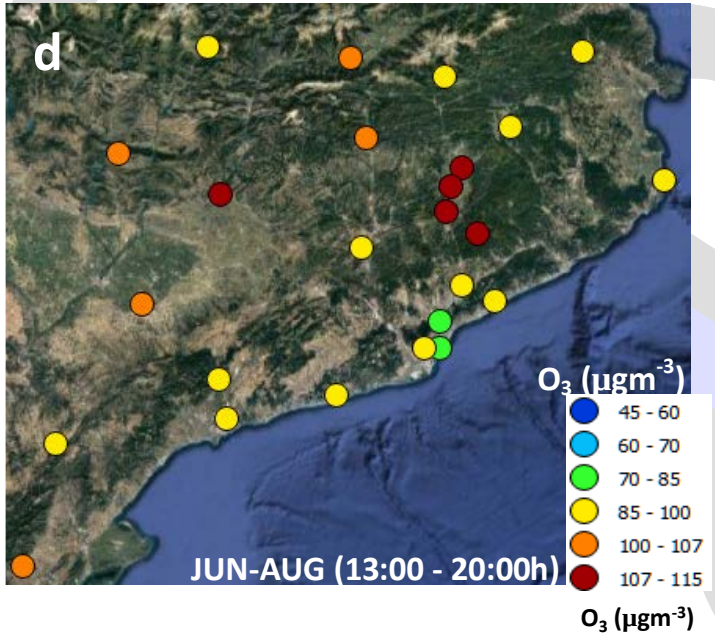
# Origin of $O_3$ in Spain




2005-2017

## Case study 1: N of Barcelona-Vic




Tesis Final de Máster Jordi Massagué (Máster Enginyeria Ambiental, UPC-IDAEA-CSIC)

# Origin of $O_3$ in Spain

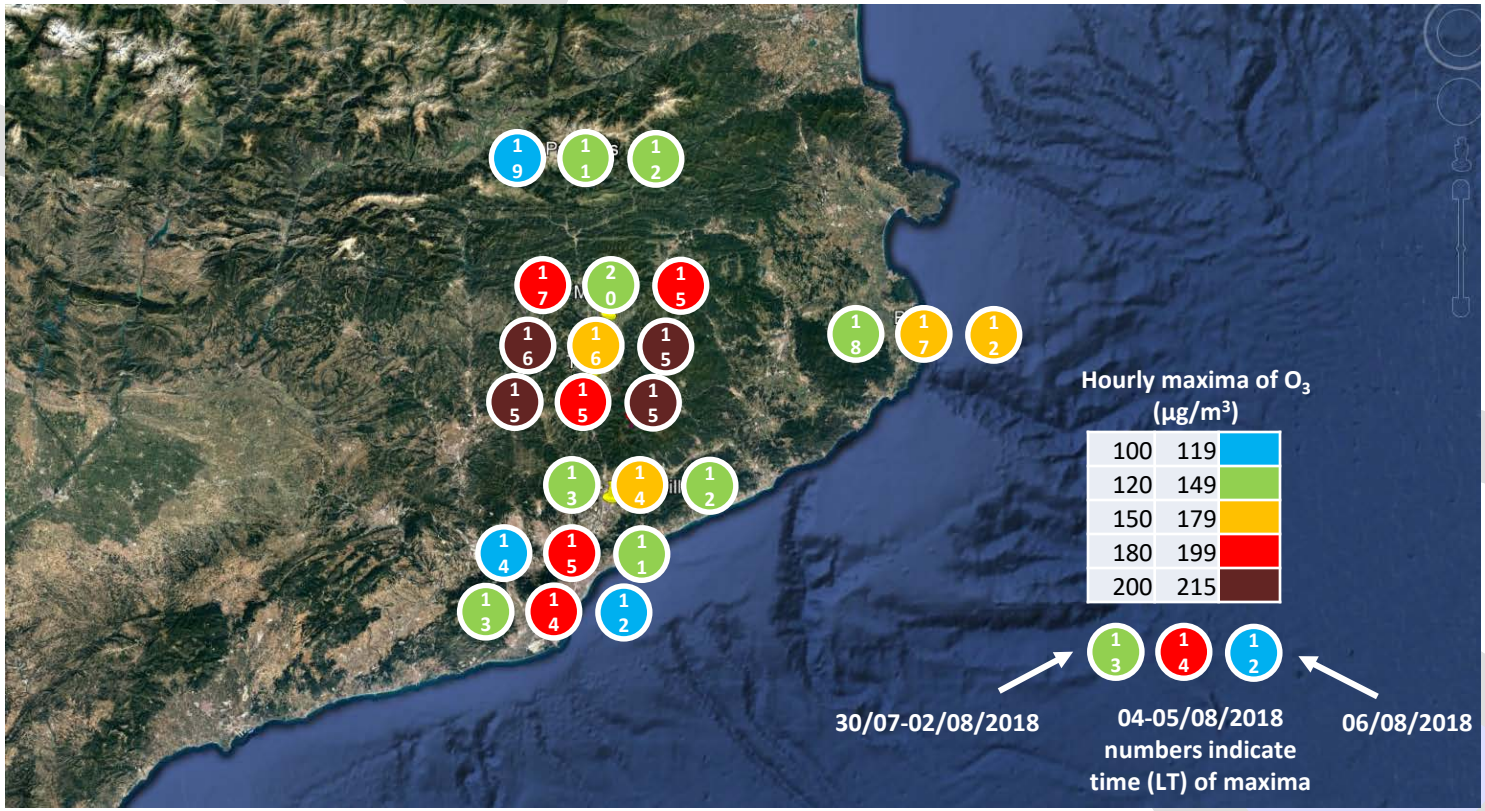
## Case study 1: N of Barcelona-Vic

### 2005-2017 (mean April-September)

| $O_3$ APR-SEP | type | period | years | initial concentration | %/year | %/year min | %/year max | %/period | units/year | units/year min | units/year max | units/period | p-Value |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CTL | UB | 2006-2017 | 13 | 45,2 | 1,4 | -0,6 | 2,4 | 17,8 | 0,6 | -0,3 | 1,1 | 8,4 | + |
| MON | SUT | 2005-2017 | 13 | 41,5 | 3,2 | 1,3 | 6,0 | 42,1 | 1,3 | 0,6 | 2,2 | 16,5 | ** |
| MAN | SUB | 2006-2017 | 12 | 58,0 | 1,3 | 0,0 | 2,5 | 15,9 | 0,7 | 0,0 | 1,3 | 8,9 | * |
| TON | RB | 2005-2017 | 13 | 73,0 | 0,3 | -0,5 | 1,4 | 3,7 | 0,2 | -0,4 | 0,9 | 2,7 | |
| VIC | SUB | 2005-2017 | 13 | 61,7 | 0,3 | -0,3 | 1,7 | 4,1 | 0,2 | -0,2 | 1,0 | 2,5 | |
| BEG | RB | 2005-2017 | 13 | 88,5 | -0,5 | -1,0 | 0,0 | -6,1 | -0,4 | -0,9 | 0,0 | -5,6 | |
| BdC | RB | 2005-2017 | 13 | 76,7 | -1,6 | -2,1 | 0,0 | -20,5 | -1,2 | -1,8 | 0,0 | -15,9 | + |
| BER | SUB | 2008-2017 | 10 | 72,3 | 0,7 | -0,2 | 2,5 | 7,2 | 0,5 | -0,2 | 1,8 | 5,4 | |
| AGU | RB | 2005-2017 | 13 | 88,9 | -1,1 | -1,6 | -0,2 | -13,8 | -0,9 | -1,4 | -0,1 | -12,2 | * |
| STP | RB | 2005-2017 | 13 | 68,7 | -1,4 | -2,6 | -0,8 | -18,0 | -0,9 | -1,8 | -0,5 | -12,3 | *** |
| MAT | UB | 2006-2017 | 12 | 71,6 | 0,4 | -0,3 | 1,3 | 4,9 | 0,3 | -0,2 | 0,9 | 3,5 | + |
| MNR | UT | 2005-2017 | 13 | 45,6 | 2,6 | 1,8 | 3,5 | 33,7 | 1,3 | 0,9 | 1,6 | 16,3 | *** |
| PON | RB | 2005-2017 | 13 | 72,0 | -0,1 | -0,8 | 1,1 | -1,5 | -0,1 | -0,6 | 0,8 | -1,1 | |
| LSE | RB | 2005-2017 | 13 | 92,8 | -0,2 | -0,7 | 0,3 | -2,7 | -0,2 | -0,7 | 0,3 | -2,5 | |
| CON | SUI | 2005-2017 | 13 | 58,9 | 0,2 | -0,4 | 1,6 | 2,9 | 0,2 | -0,2 | 1,0 | 2,0 | |
| GAN | RB | 2005-2017 | 13 | 74,3 | 0,5 | -0,4 | 2,0 | 6,1 | 0,4 | -0,4 | 1,6 | 5,1 | |
| VGe | SUT | 2005-2017 | 13 | 65,6 | 0,4 | 0,0 | 0,9 | 5,4 | 0,3 | 0,0 | 0,6 | 3,6 | |
| ALC | SUI | 2005-2017 | 13 | 73,9 | 0,5 | 0,0 | 1,5 | 6,8 | 0,4 | 0,0 | 1,1 | 5,1 | * |

# Origin of $O_3$ in Spain

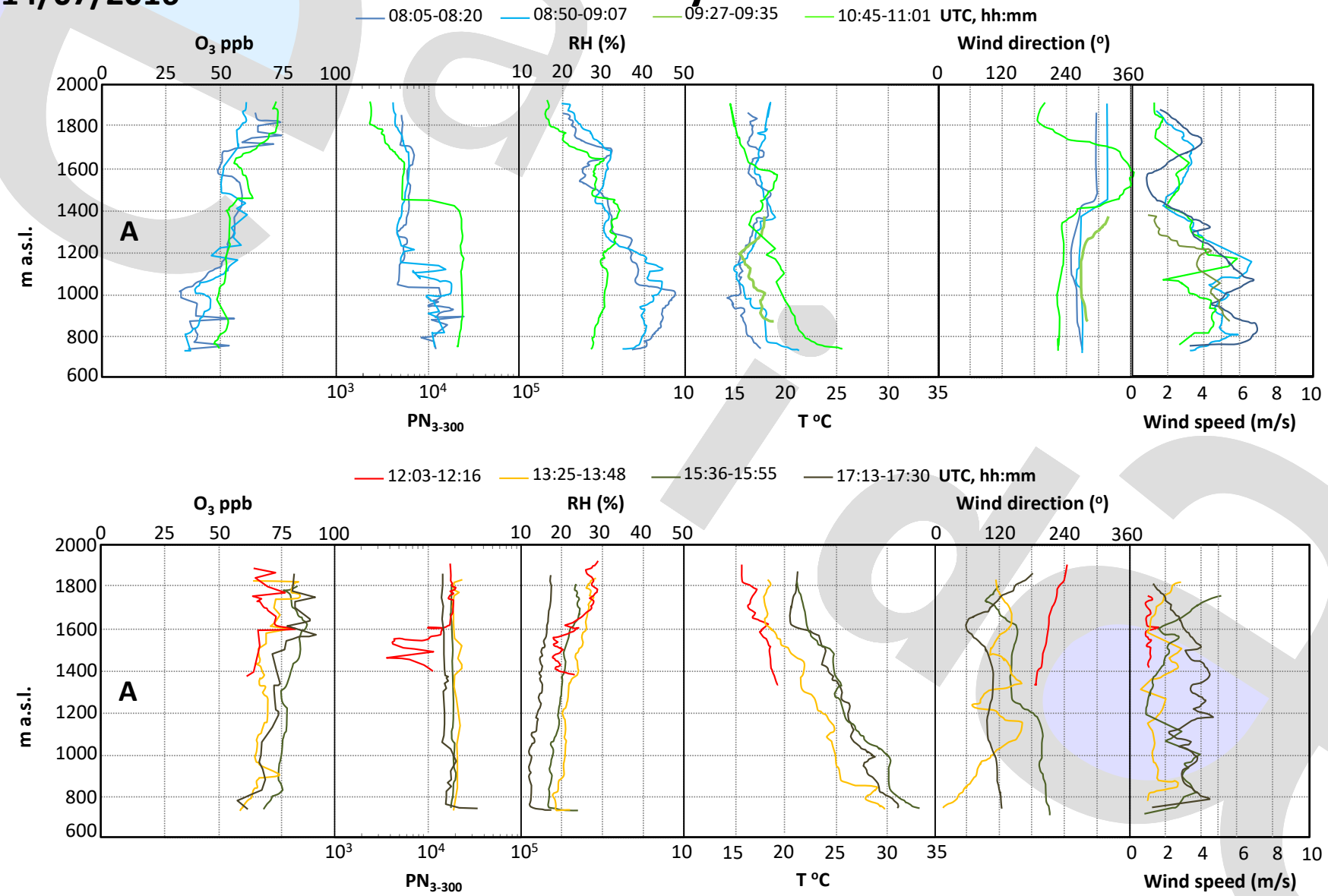
## Case study 1: N of Barcelona-Vic



# Origin of $O_3$ in Spain

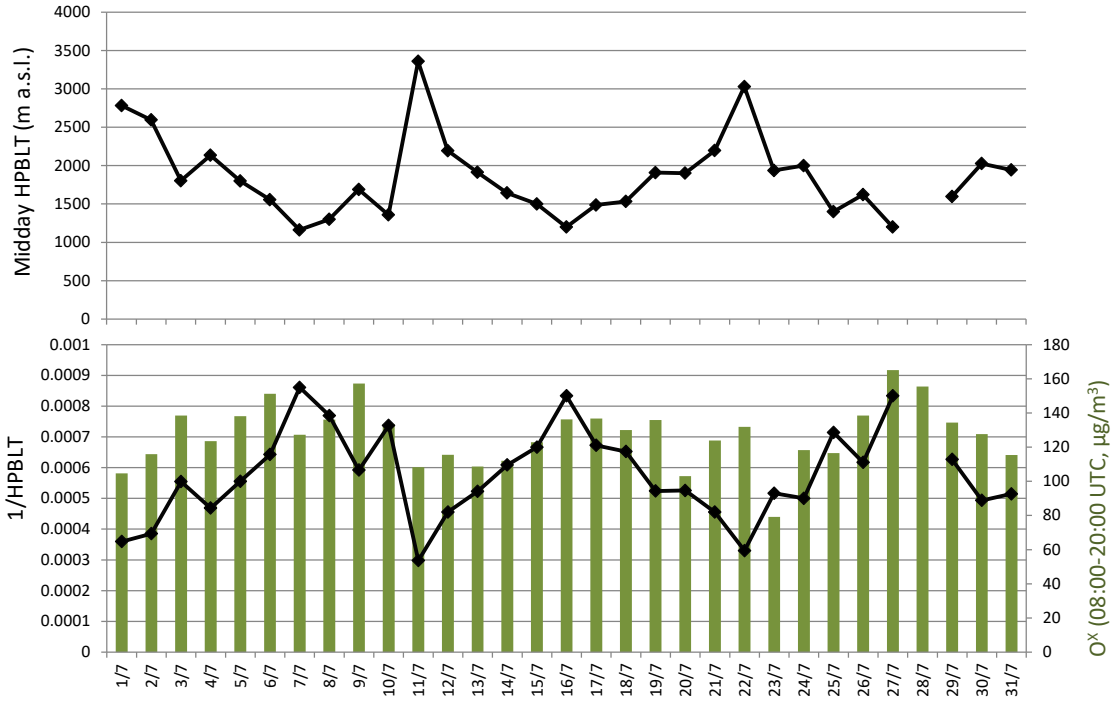
## 14/07/2016

## Case study 2: Madrid



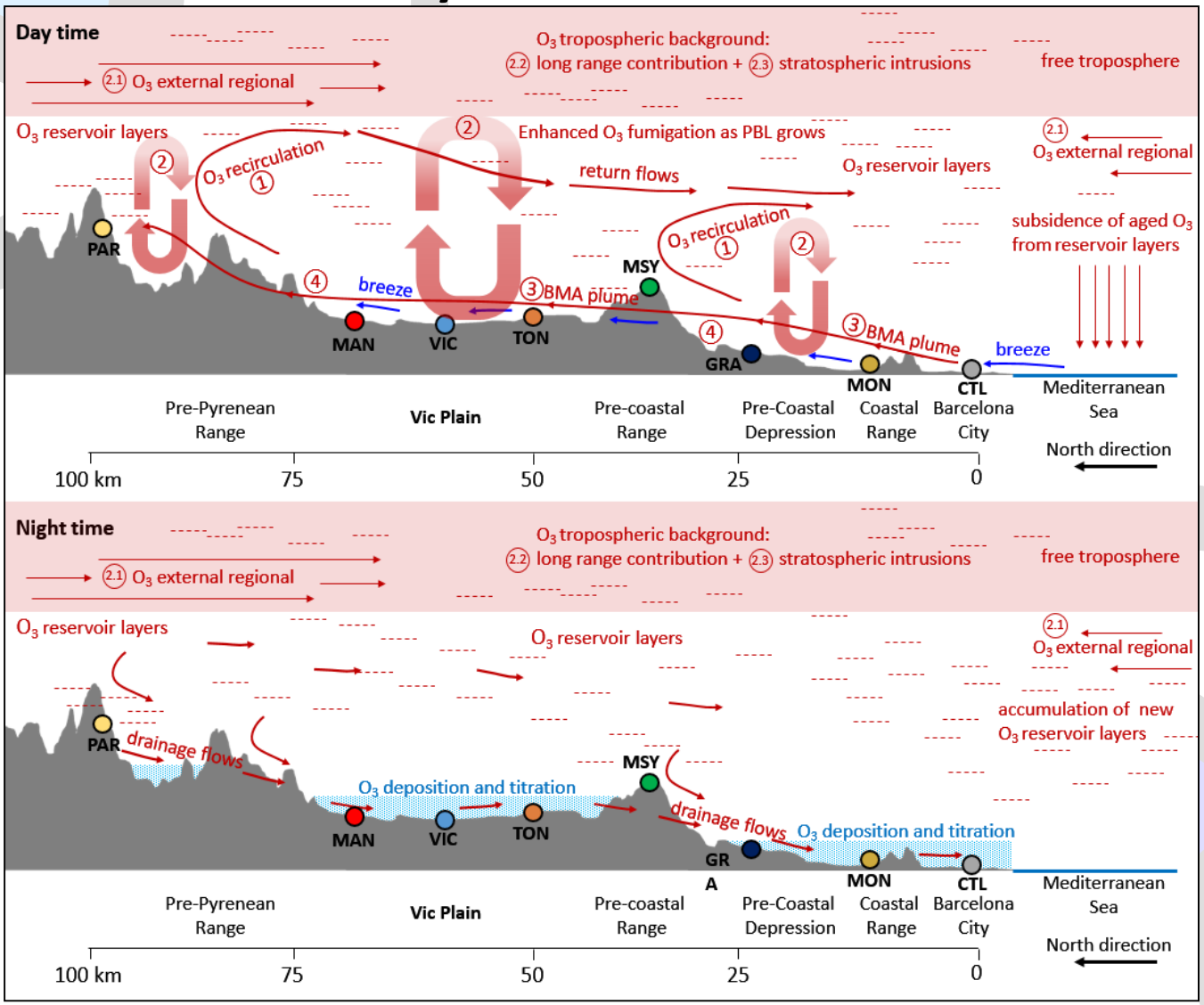
# Origin of $O_3$ in Spain

## Case study 2: Madrid



# Origin of $O_3$ in Spain

## Case study 1: N of Barcelona-Vic

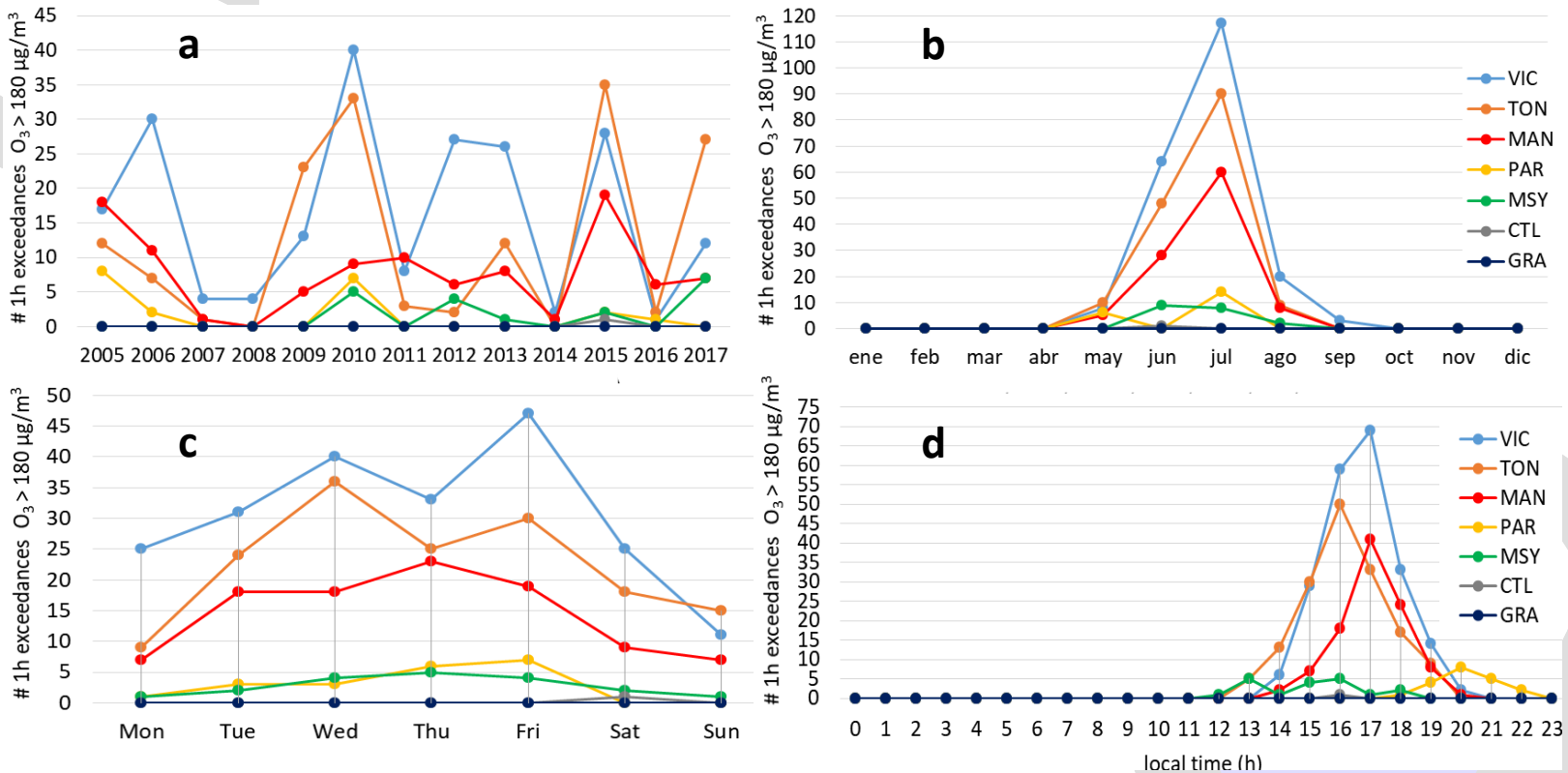



Tesi Final de Màster Jordi Massagué (Màster Enginyeria Ambiental, UPC-IDAEA-CSIC)

# Origin of $O_3$ in Spain

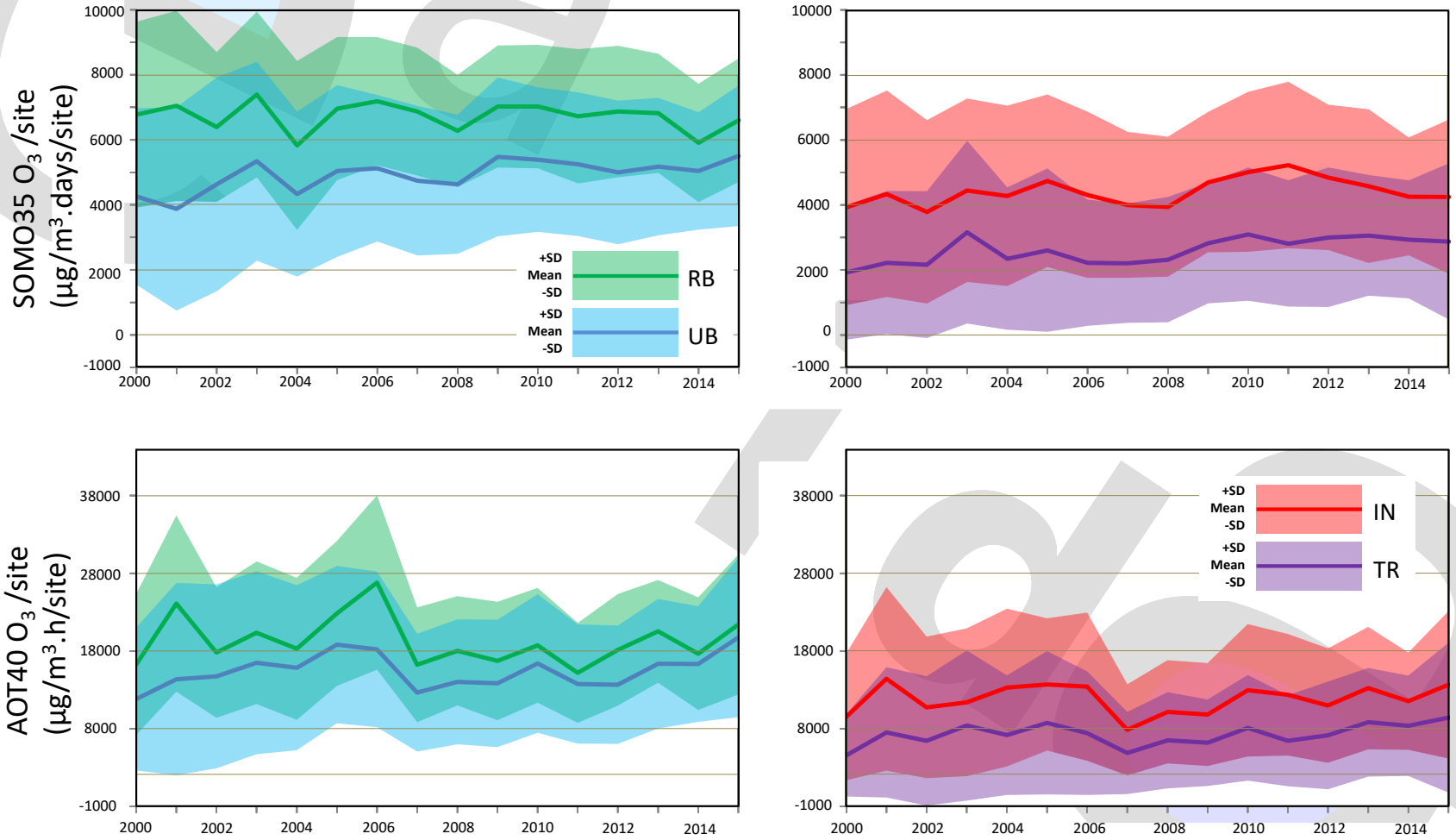
## Case study 1: N of Barcelona-Vic

### Valores medios 2005-2017




Tesis Final de Master Jordi Massagué (Master Ingeniería Ambiental, UPC-IDAEA-CSIC)

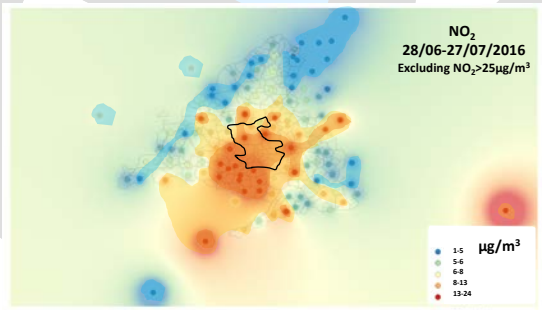
# Levels and time-trends of $O_3$ in Spain

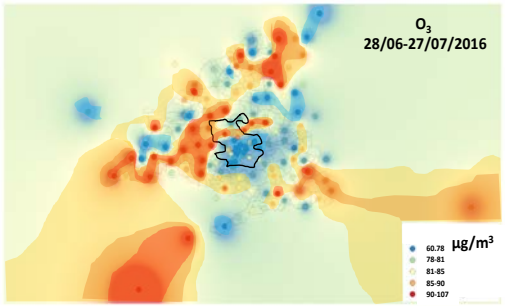


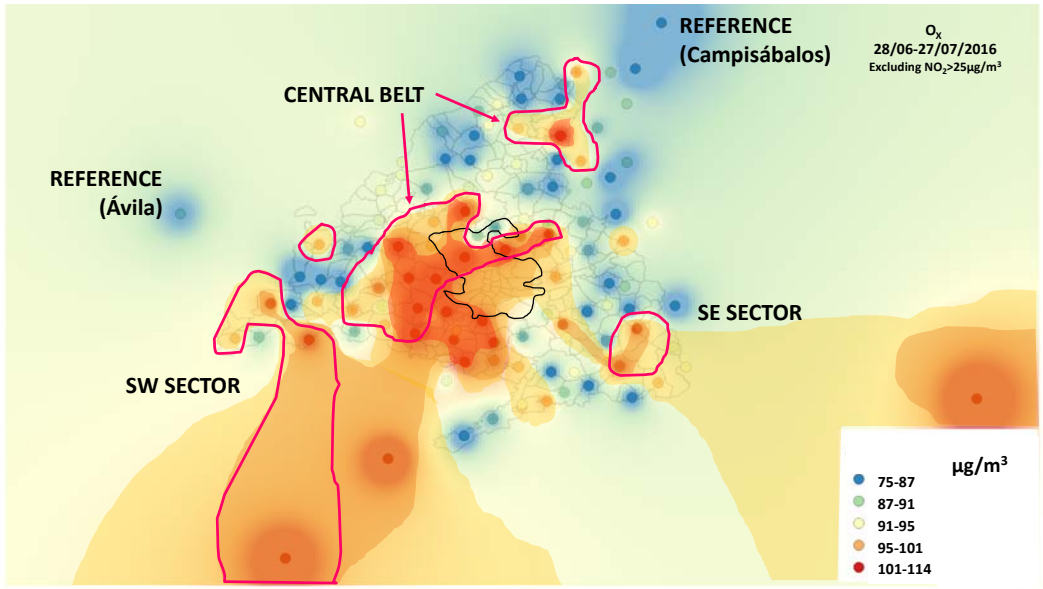

*Querol X. et al., Science of the Total Environment 572 (2016) 379–389*

# Origin of $O_3$ in Spain

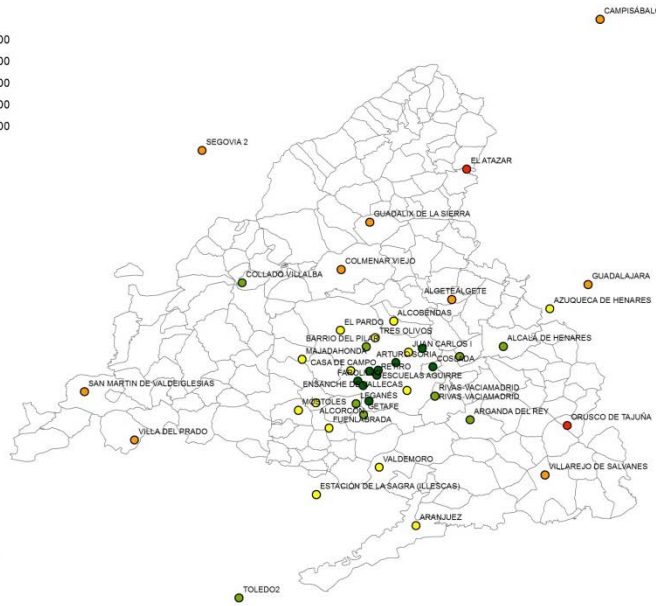
## Case study 2: Madrid








JULY 2016