2010-2020 O_3 variability & 2019-2020 measurements of VOCs-O_3 precursors in Spain

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TFMM-EMEP, May 11-12, 2020

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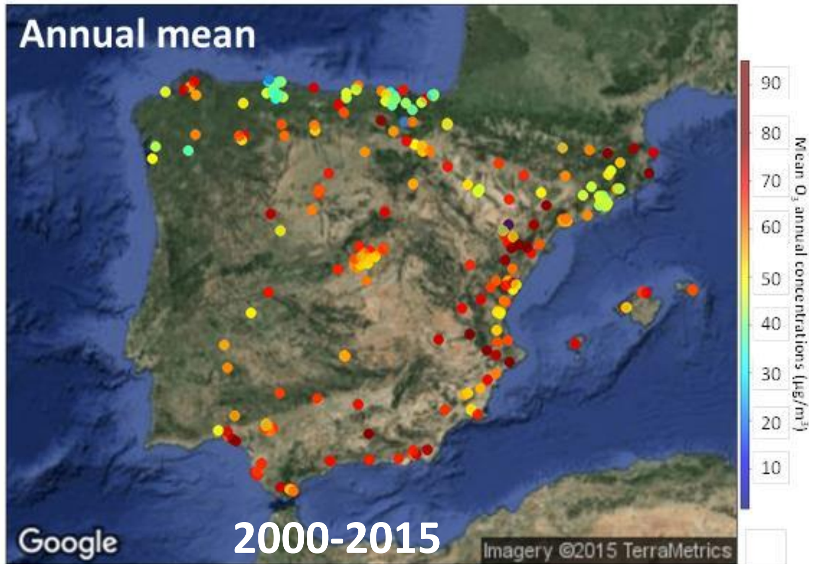
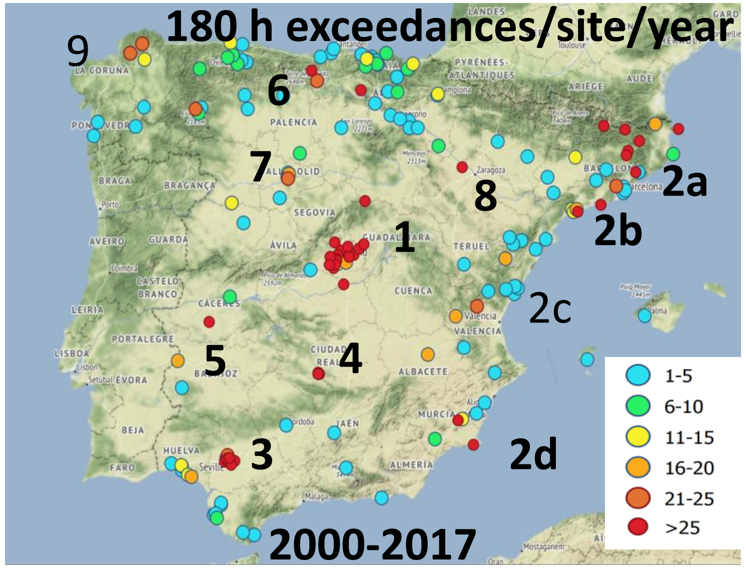
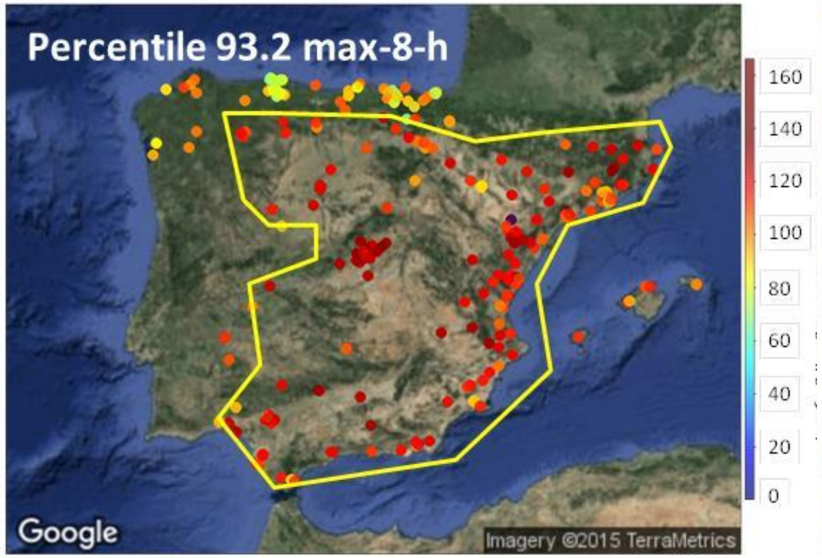
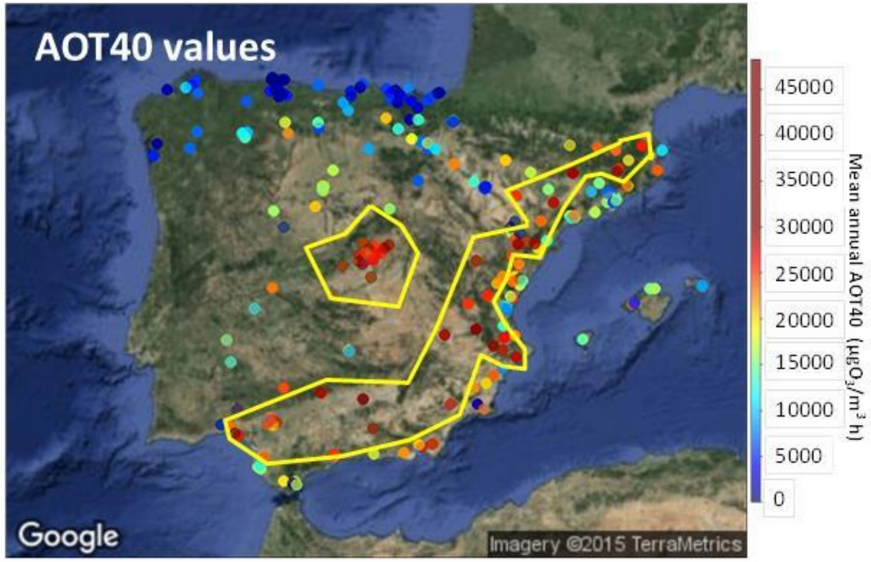
Introduction

- A large proportion of the Spanish territory exceeding the human protection target
- Gradients N-**C-S** and W-**C-E**
- Complex phenomenology (Millán et al, 1997 and subsequent studies)
- Relevant transboundary contributions
- But local contributions relevant in acute episodes
- Up to now most modelling outputs indicating no effects of local measures









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

Objectives (O_3 National Plan Team)

Partially in this presentation

- Trend analysis
  - Querol et al (2016) Sci Total Environ evaluated 2000-2015 O_3 trends in Spain. Here we updated to 2000-2020, but emphasis on 2010-2020
  - Trend analysis 2000-2019 and 2010-2019
  - 2020 evaluated separately because COVID19 effect on AQ
  - Lessons learned for O_3
- Experimental studies of O_3 acute episodes in different basins using airborne and/or meteorological tools
- Evaluating VOCs concentrations in different basins of Spain
- Evaluating emission sources of VOCs and NOx and BAT implemented in different basins
- Feeding modelling tools for sensitivity analysis with data and know how from prior sub-objectives
- Propose a National strategy to abate O_3 at different scales (some outside the National scale)

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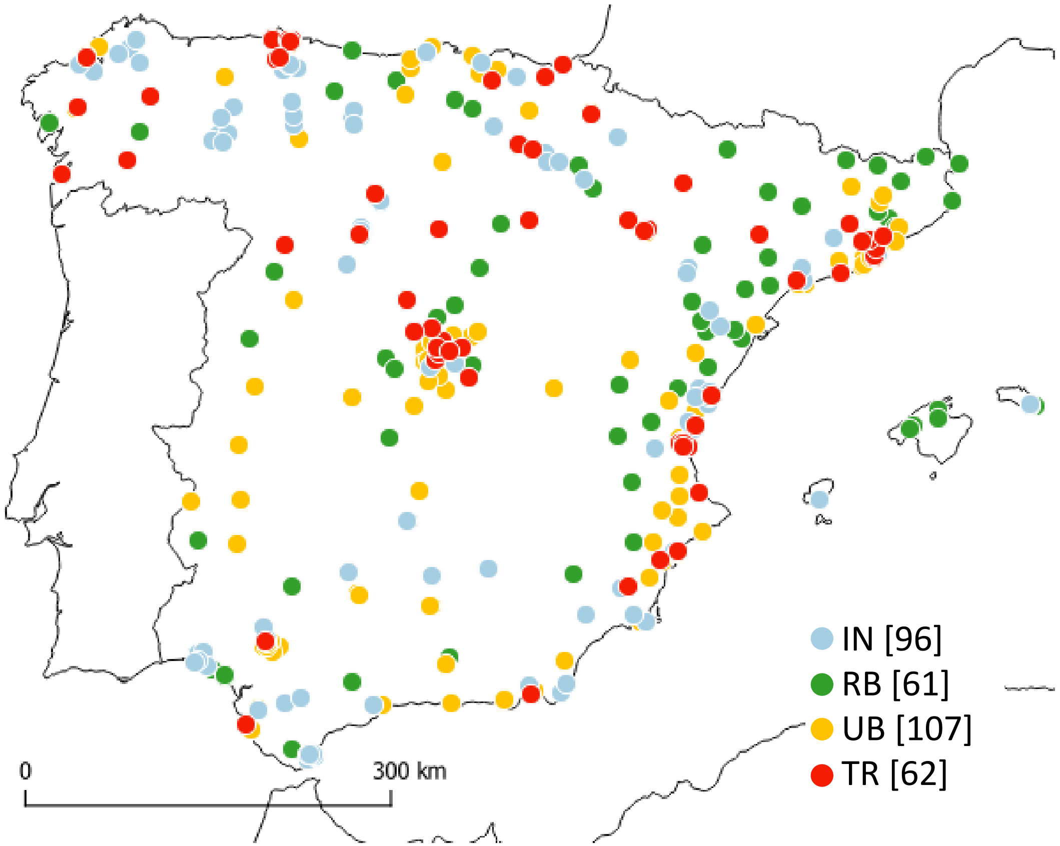
Methodology (Time Series 2010-2020)

1. 2010-2019 O_3 data sets & AQ sites



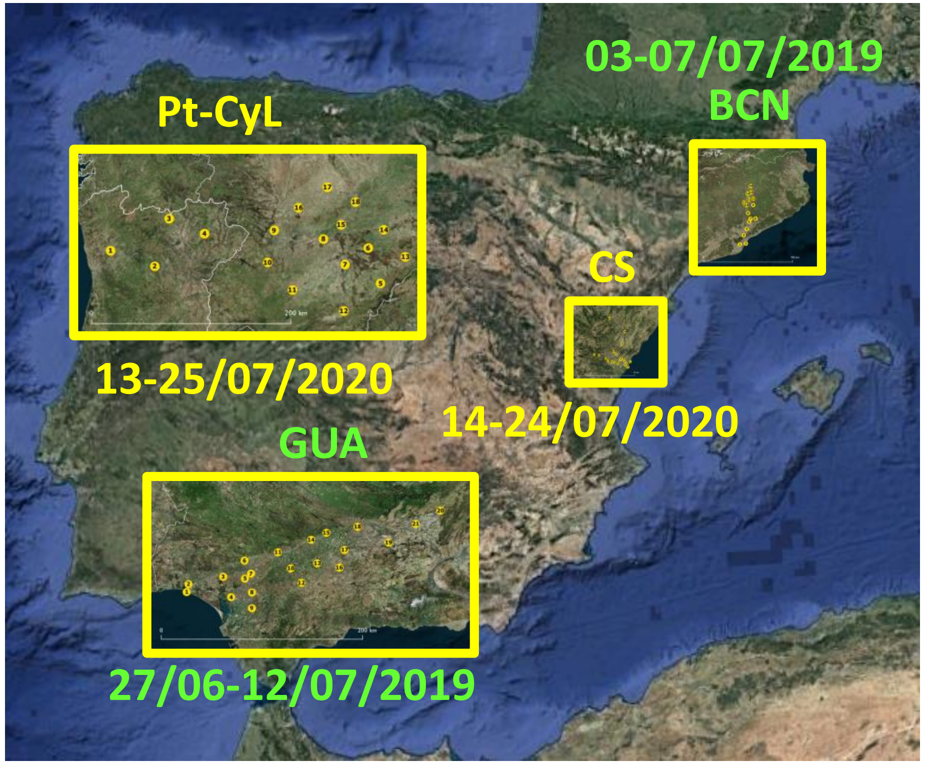
Total 326 sites
Minimum 9 yrs data per indicator:

- Mean O_3: 75% availab/year [326]
- Mean O_x: 75% availab/year [231]
- P93.2 MDA8 : 75% availab/year [226]
- N. exceedances 1h>180µg/m^3 :75% availab/year [257]
- AOT40 (veg) : 90% availab/year (May-Jul, 8h-20h CET) [266]
- SOMO35 : 90% availab/year [226]

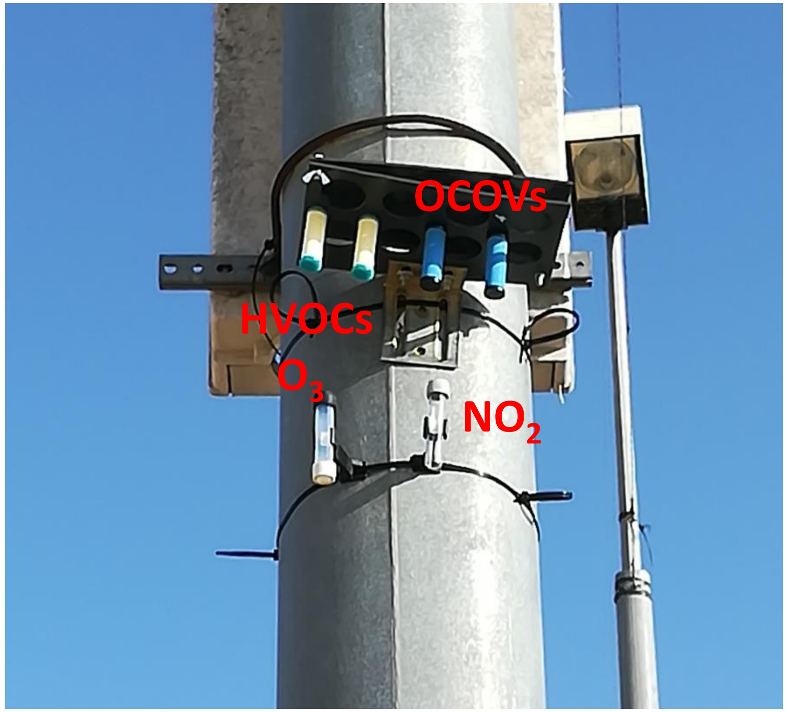
2. Lessons learnt on effect of COVID19 lockdown on O_3

Querol X. et al., 2021. Sci Total Environ. 2015-2020 and effect of COVID on AQ

Methodology (VOCs)



GC-MS



GUA 19 sites, 78 VOCs detected (45 HVOCs & 33 OVOCs)
BCN 16 sites, 65 VOCs (36HVOCss & 29 OVOCs
Pt-CyL 18 sites, 52 VOCs (39 HCOVs y 13 OVOCs)
CS 19 sites, 44 VOCs (30 HVOCs y 14 OVOCs)

Limitations
- Passive dosimeters
- <C5 not measured
- Isoprene not measured
- Indicative method
- 15 days averages

Pros
- Easily deployed
- Spatial variations

Results (Time Series 2010-2019)

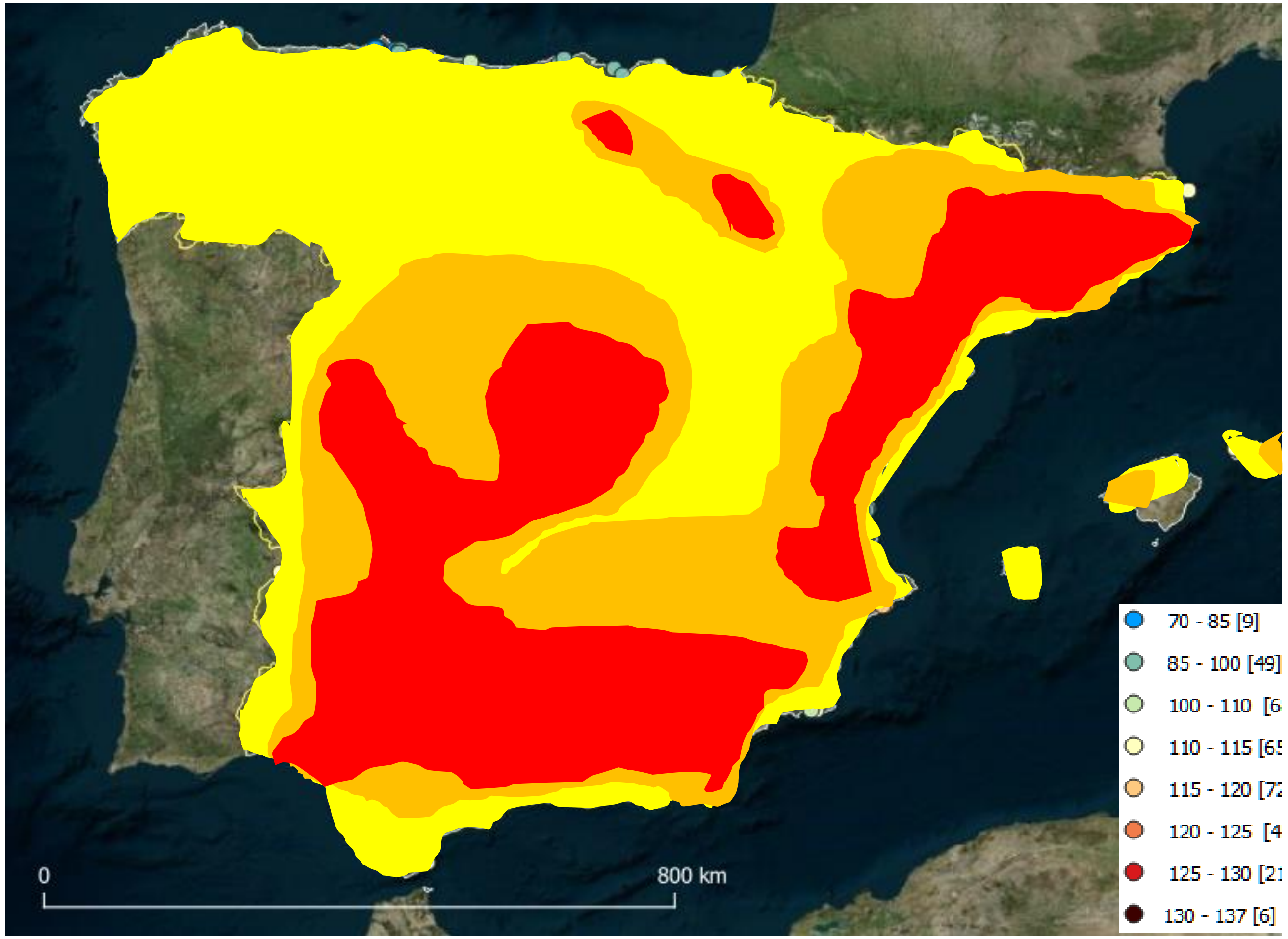
Averages 2010-2019

Exceedance of the EU AQ Health protection target value

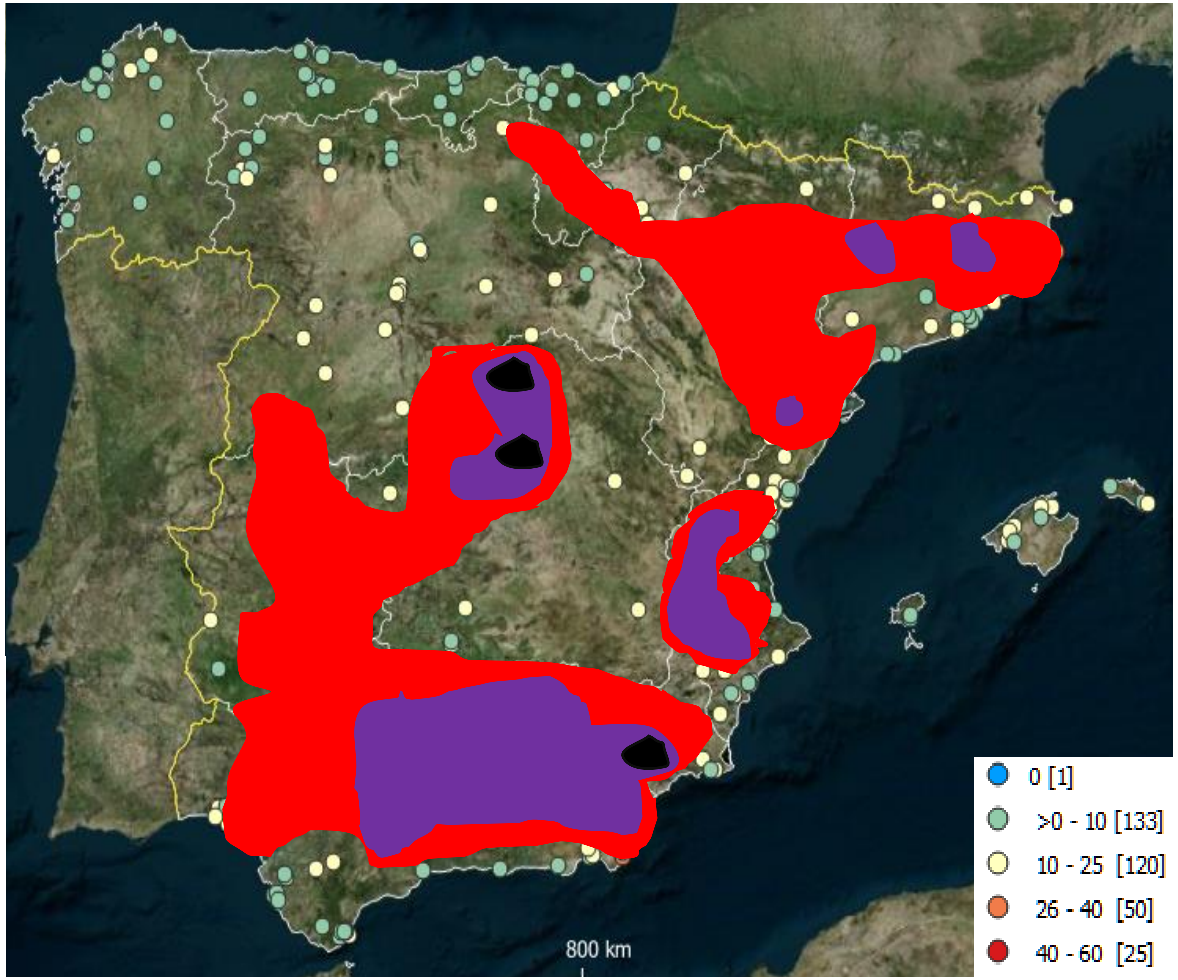
Exceedance of the WHOAQG   Close to EU AQ target value

MEASURES REQUIRED AT NATIONAL BUT ALSO EU AND EVEN LARGER SCALES

Averaged 93.2 percentile 8h-DM O_3



Averaged exceedances/yr 8h-DM O_3



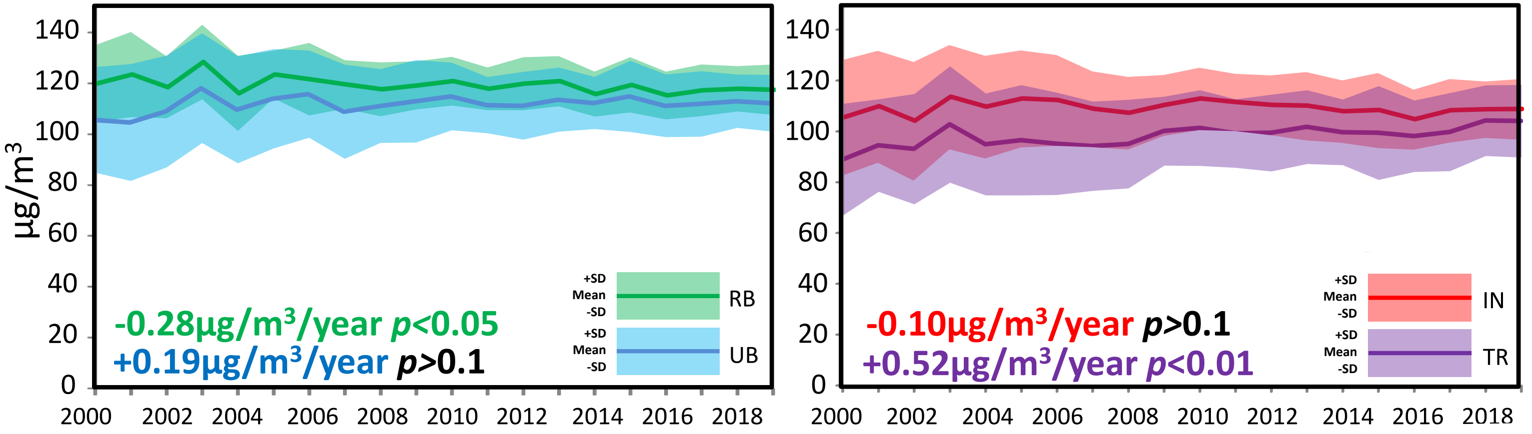
Results (Time Series 2010-2019)

Averages 2010-2019 Daily exceedances >180 µg m^{-3}

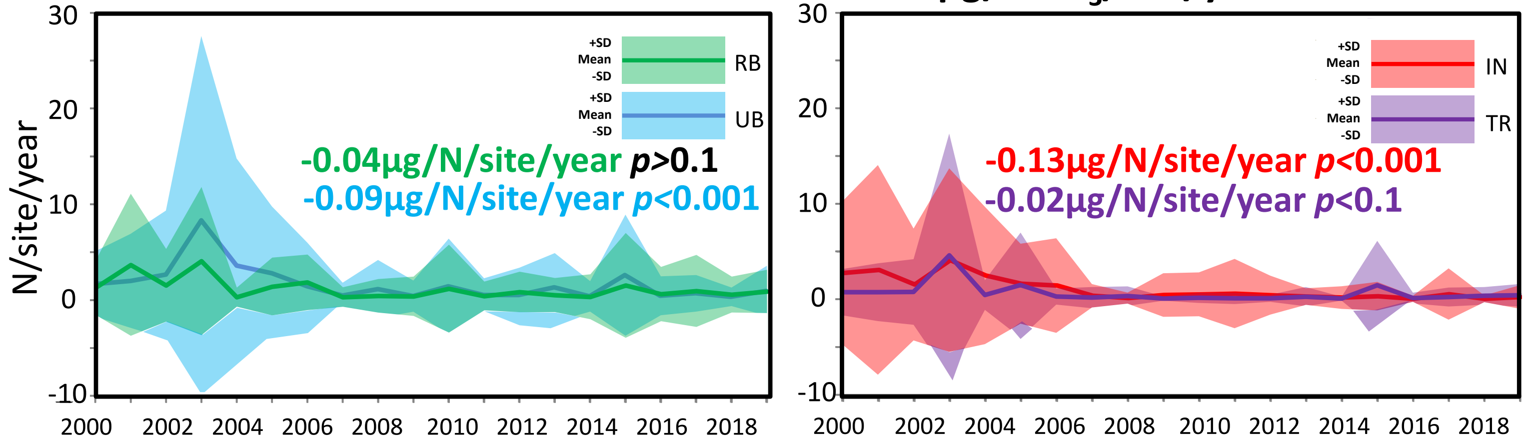
MEASURES REQUIRED AT REGIONAL & NATIONAL SCALES

Results (Time Series 2010-2019)

2000-2019 Percentile 93.2 8h µg/m³ O_3

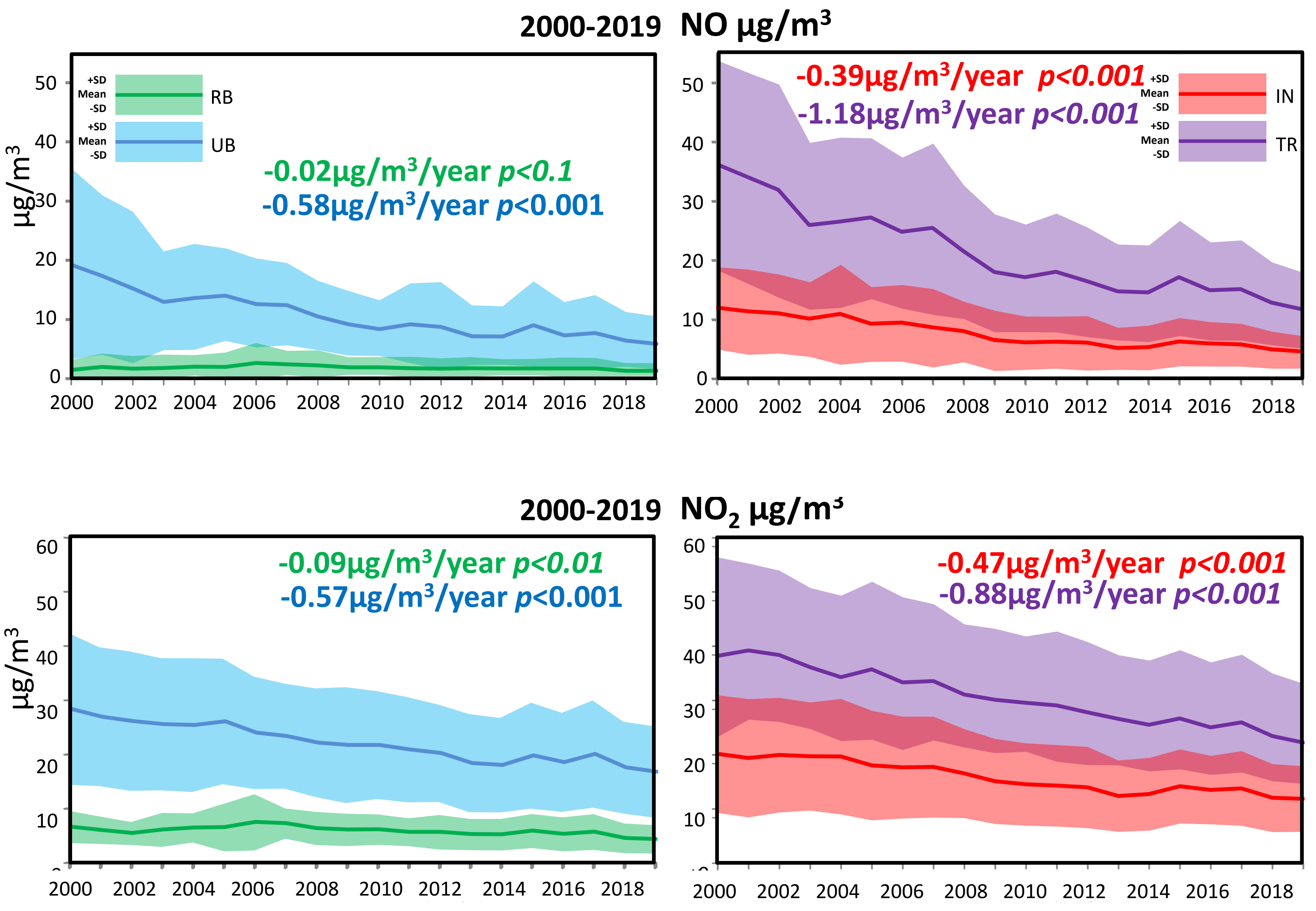


2000-2019 N exceedances 1h>180µg/m³ O_3/site/year



TRENDS 2010-2019 ≠ 2000-2019

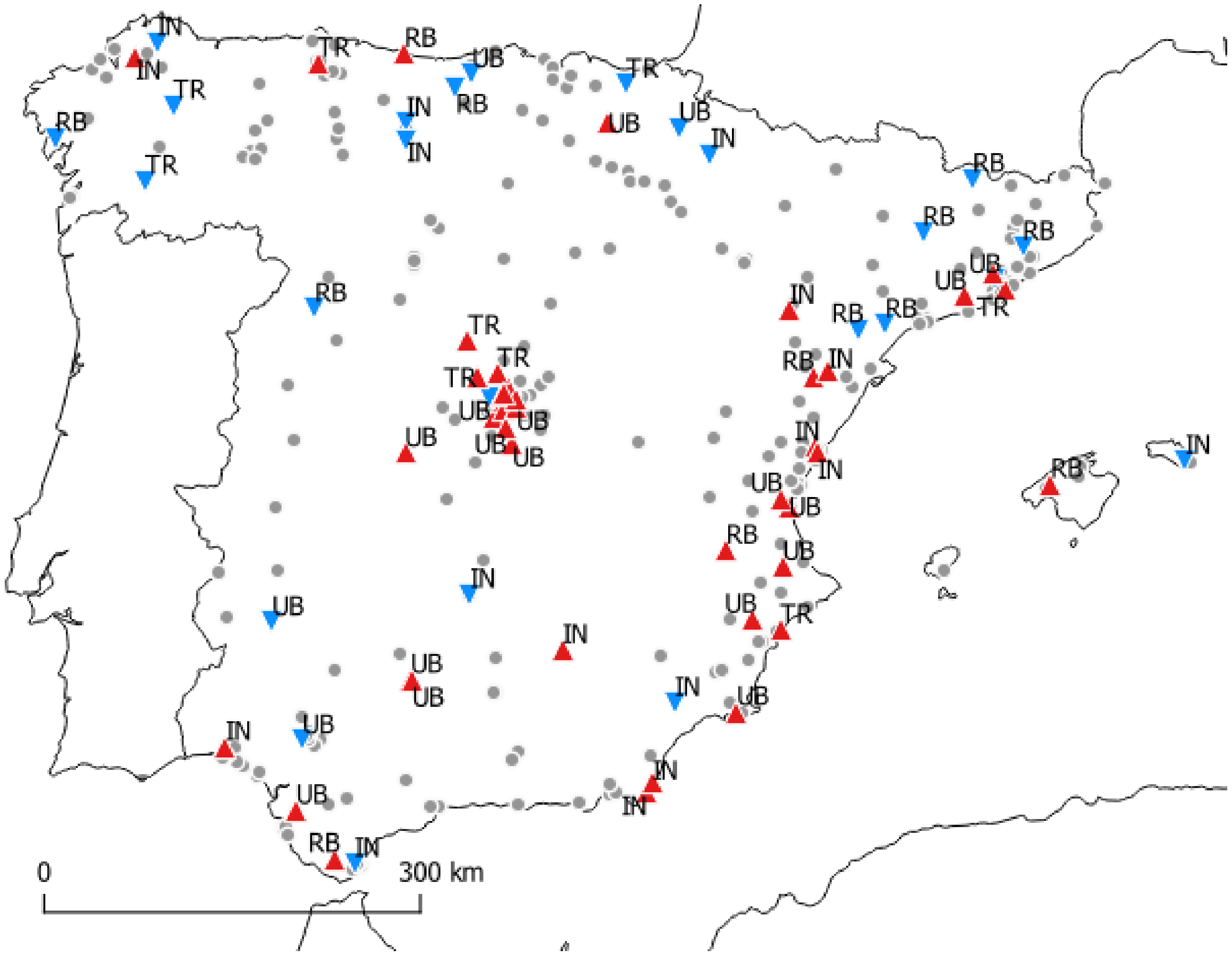
Results (Time Series 2010-2019)

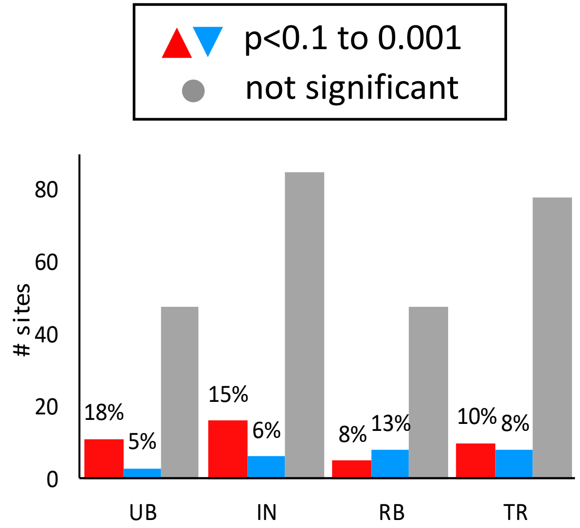


NO DECREASING LESS THAN NO_2 2010-2019 BUT MORE IN 2000-2019

Results (Time Series 2010-2019)

O_3 Annual mean 2010-2019

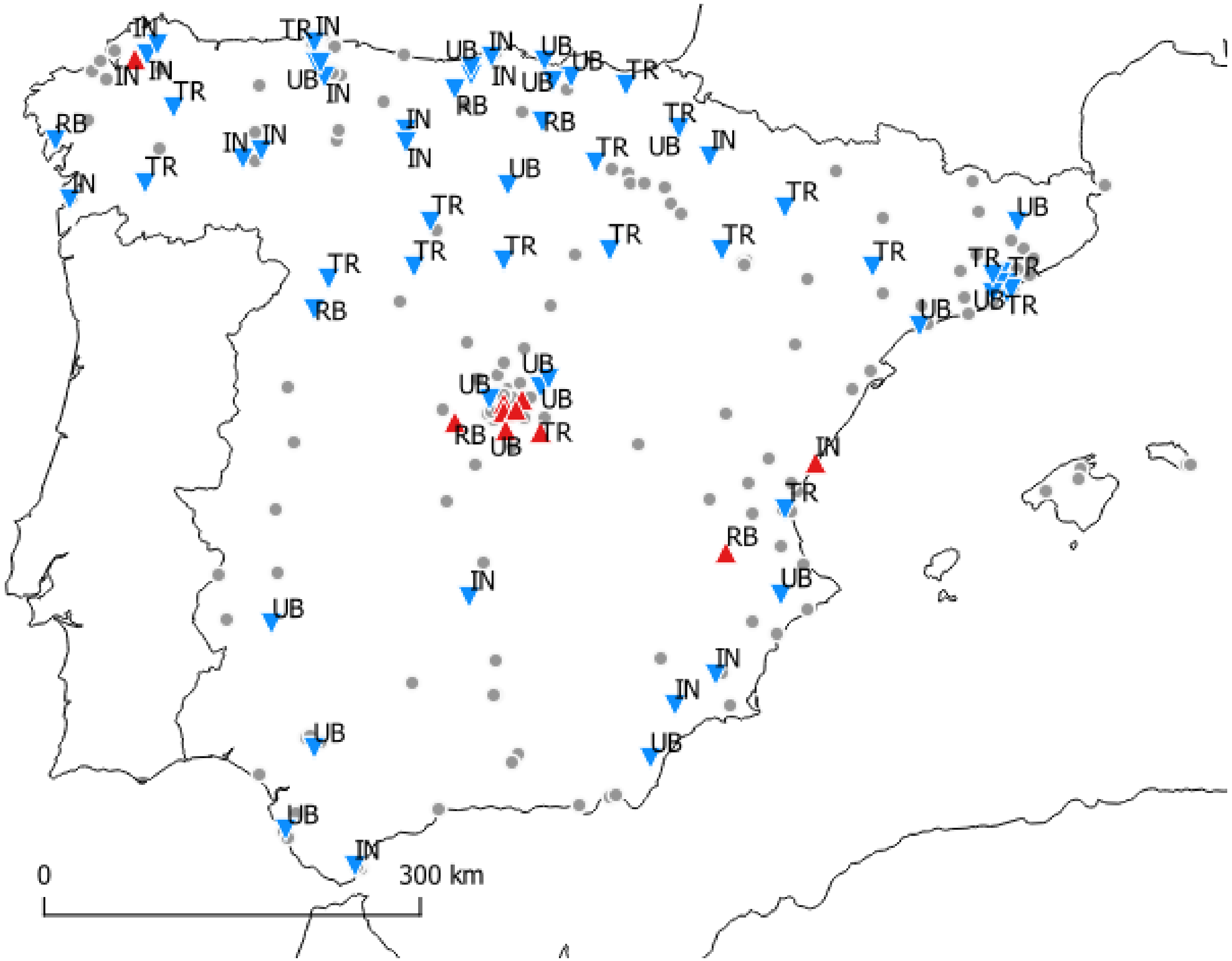


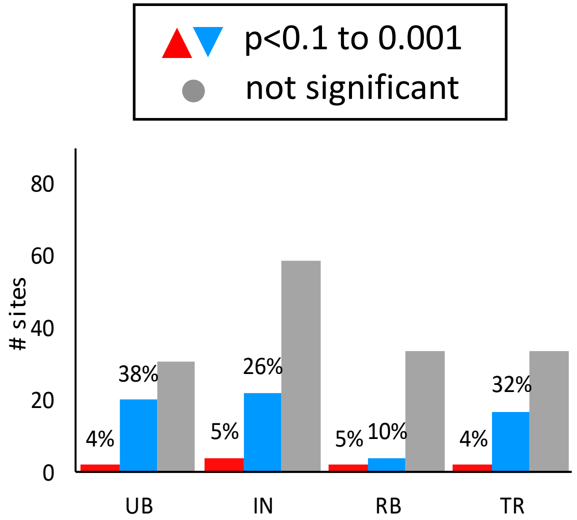


Total # sites: 326

Results (Time Series 2010-2019)

O_x Annual mean 2010-2019

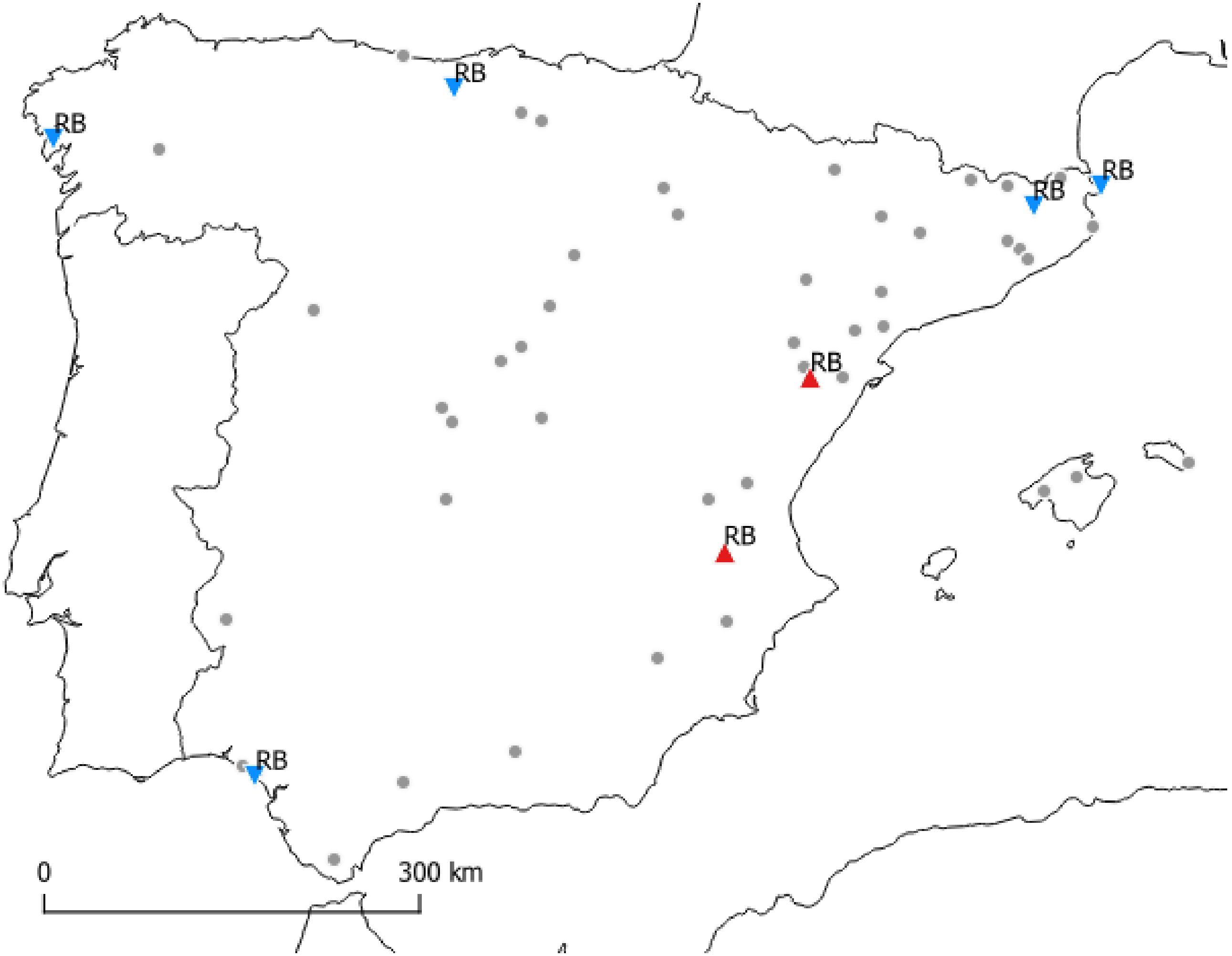


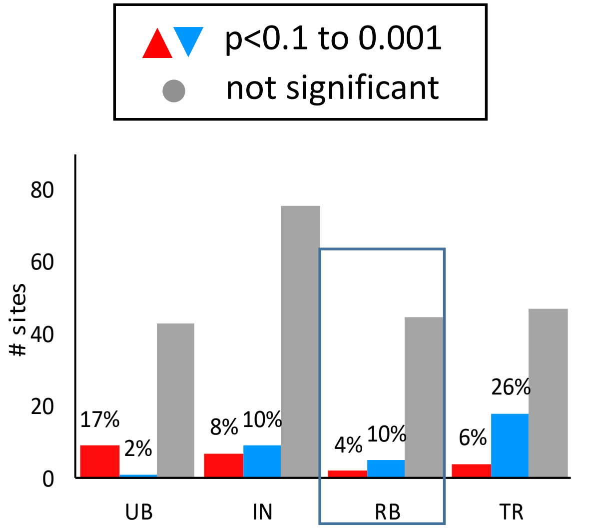


Total # sites: 231

Results (Time Series 2010-2019)

AOT40 mean 2010-2019

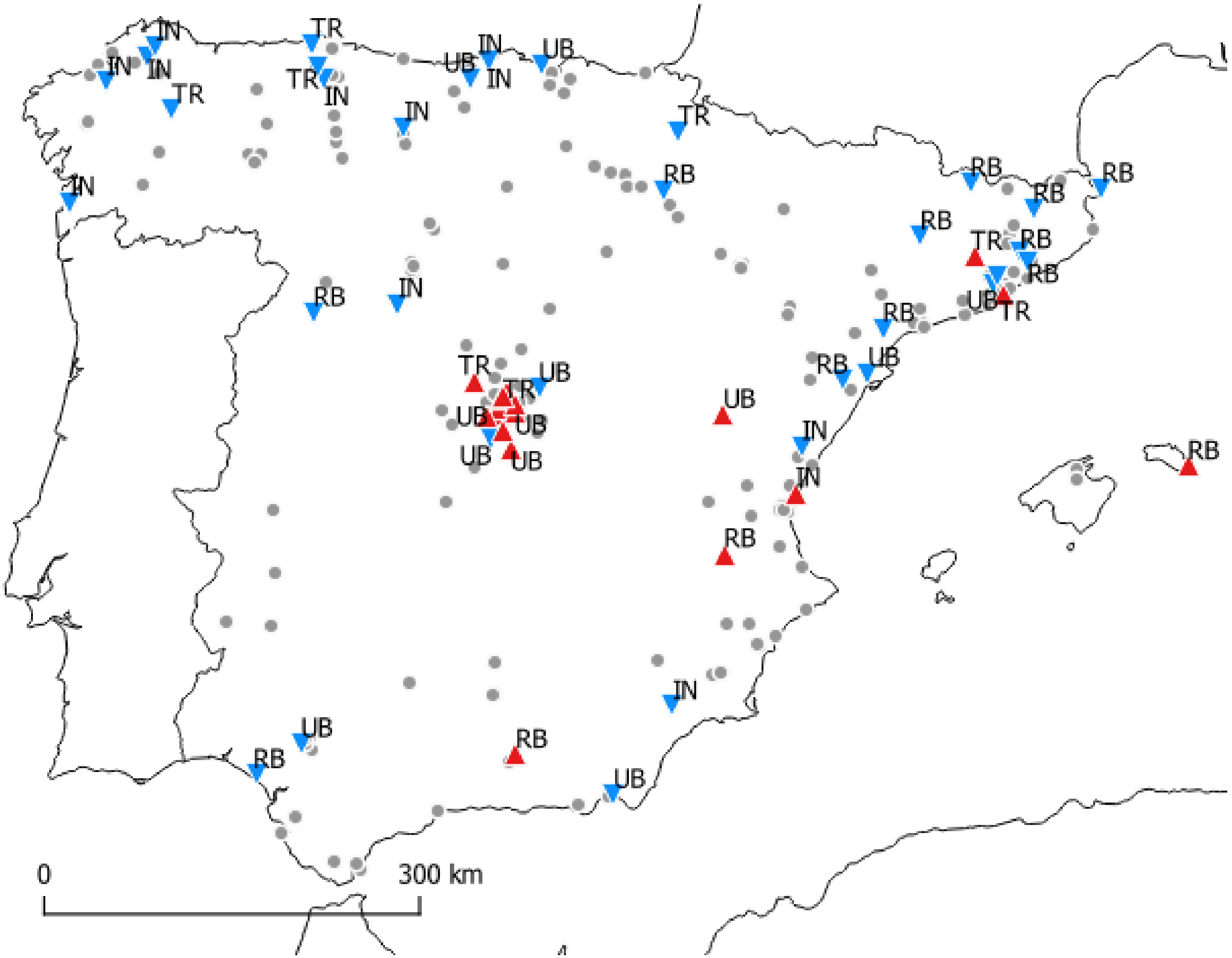


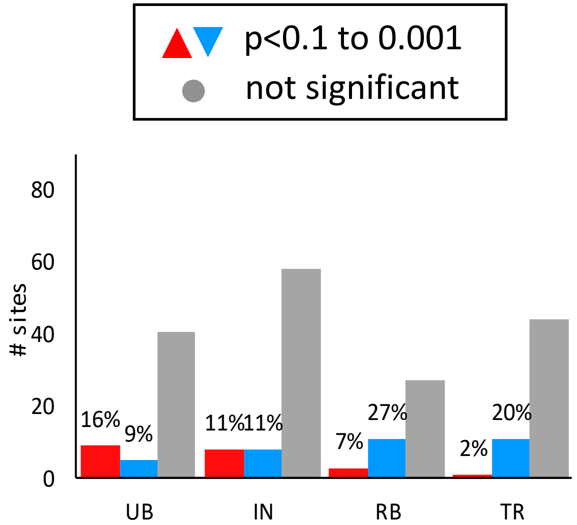


Total # sites: 266 (52 RB)

Results (Time Series 2010-2019)

P93.2 8hMDA mean 2010-2019

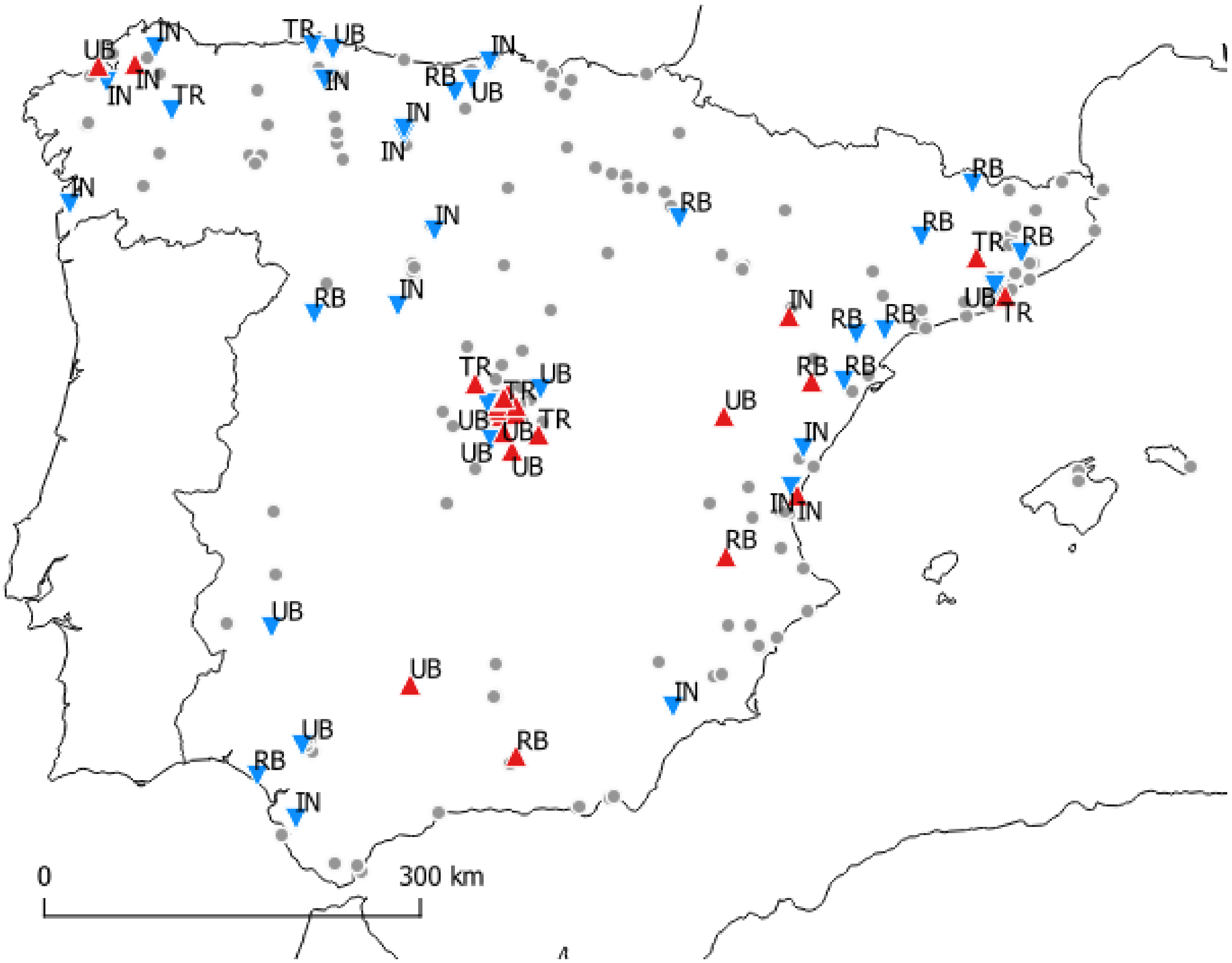


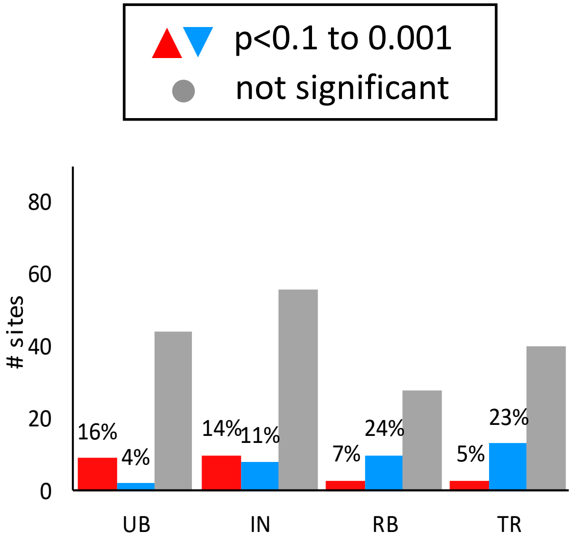


Total # sites: 226

Results (Time Series 2010-2019)

$SOMO_35$mean 2010-2019

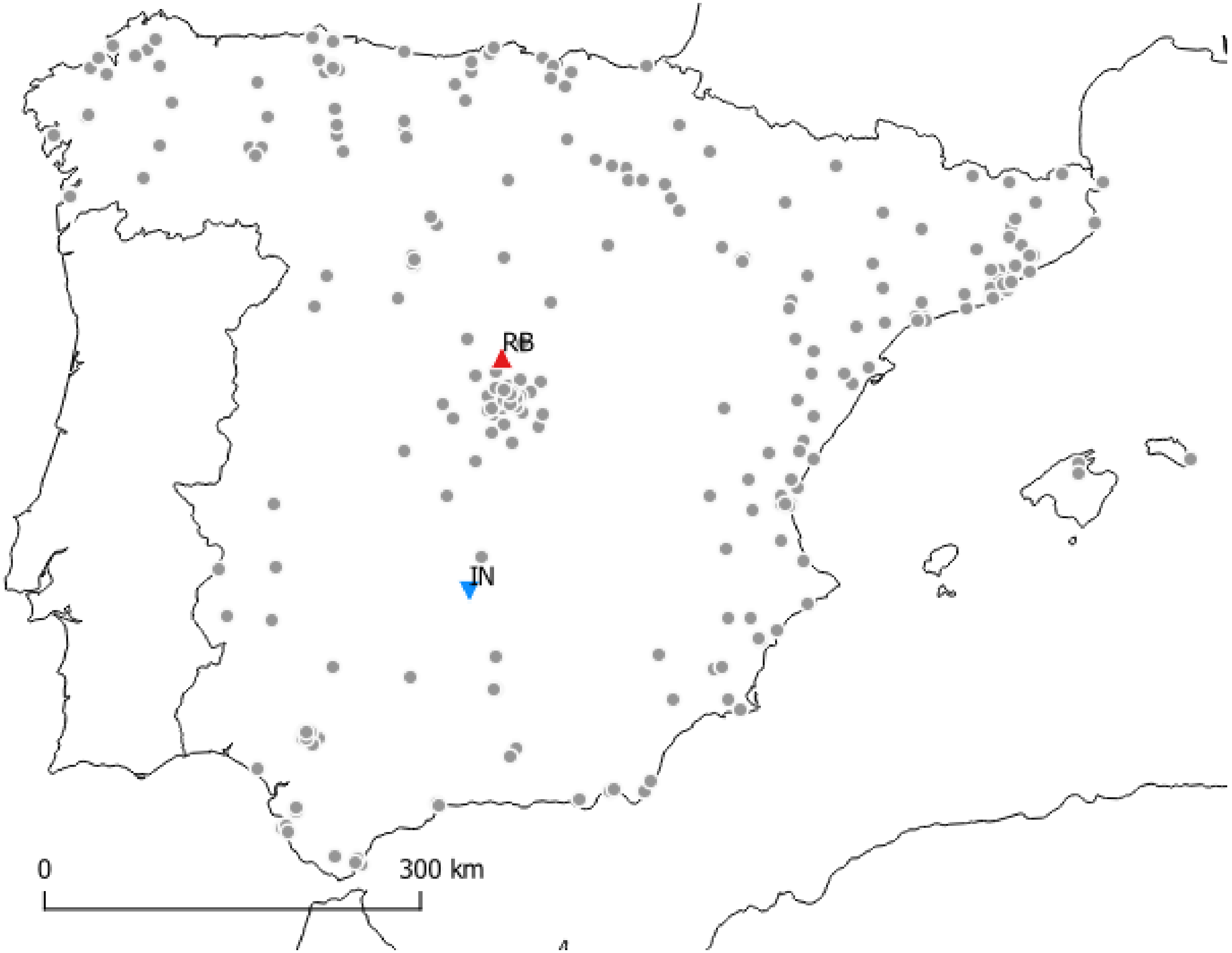


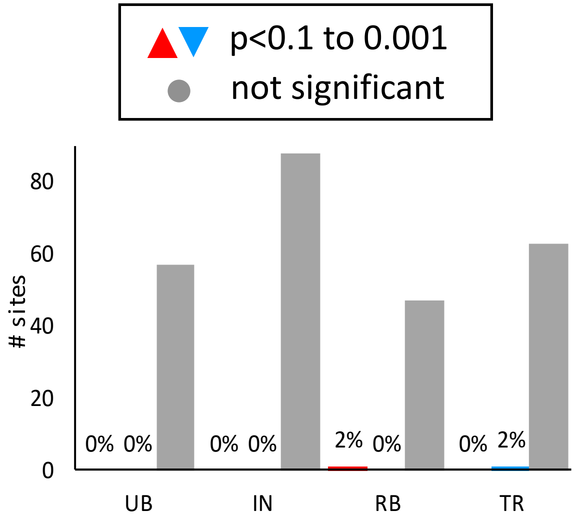


Total # sites: 226

Results (Time Series 2010-2019)

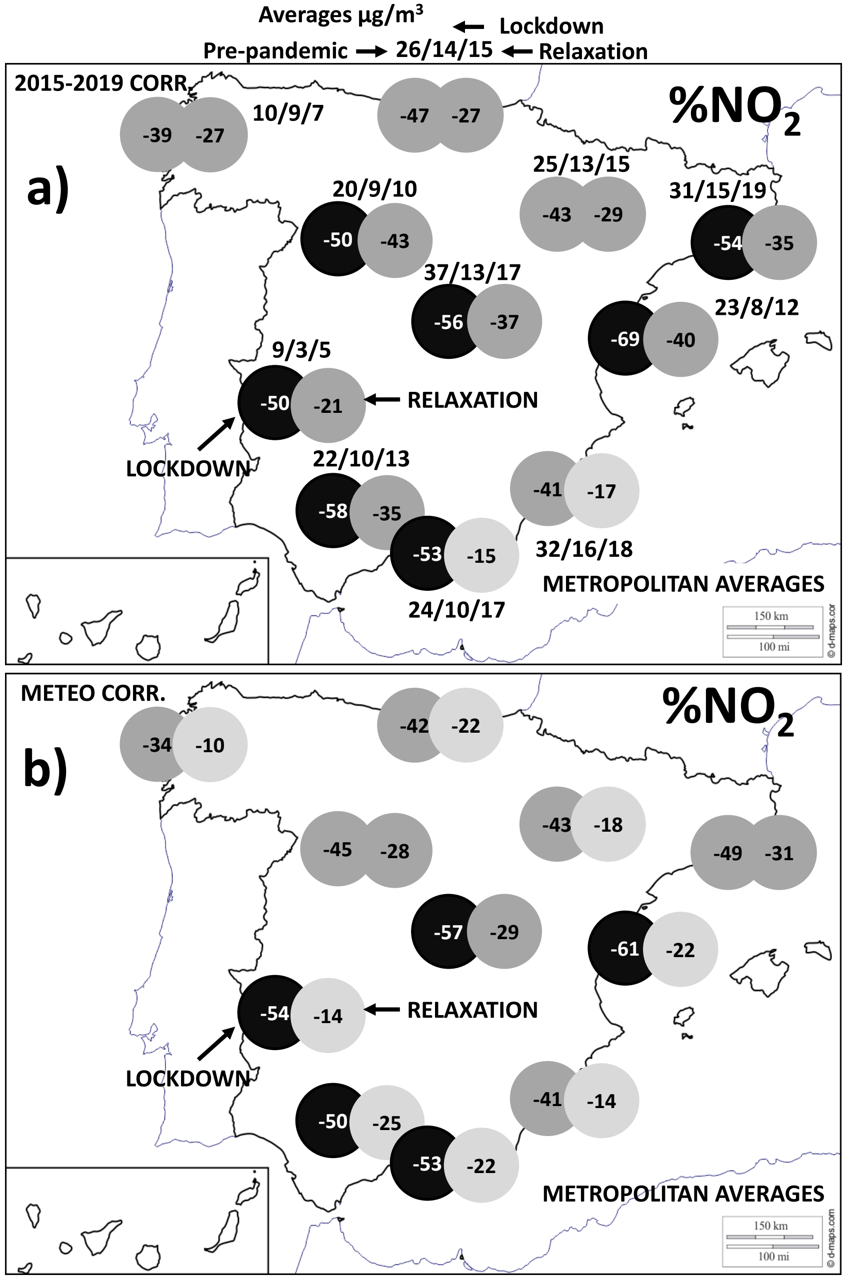
O_3 exceedances 180 information/site/year 2010-2019

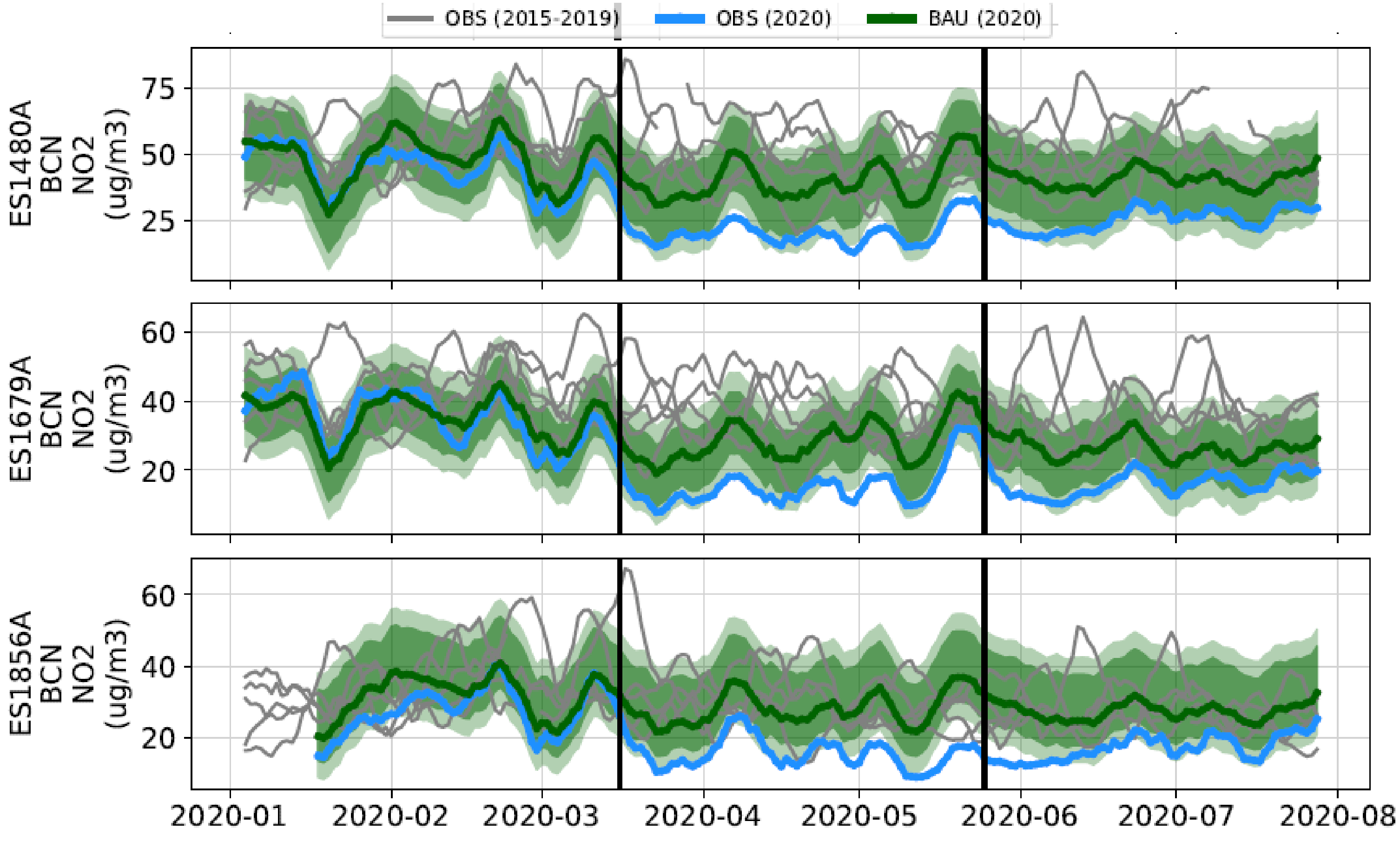




Total # sites: 257

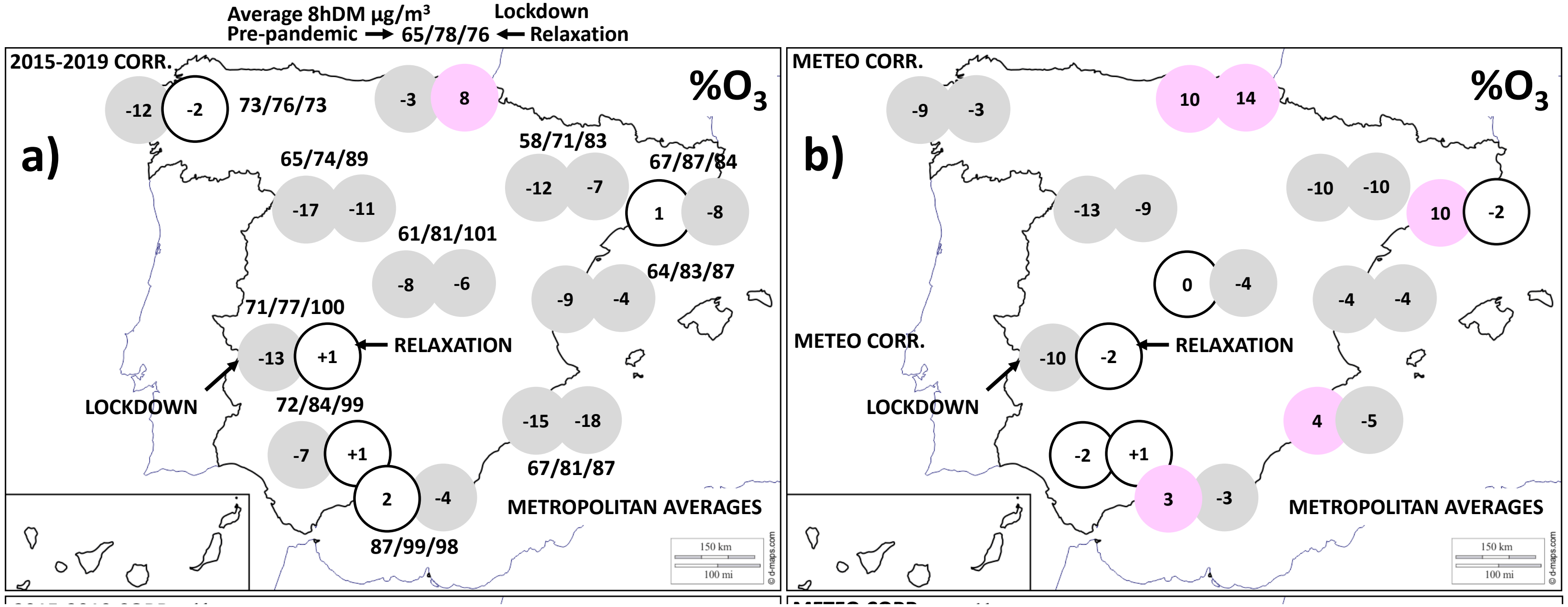
Results (Time Series 2020)





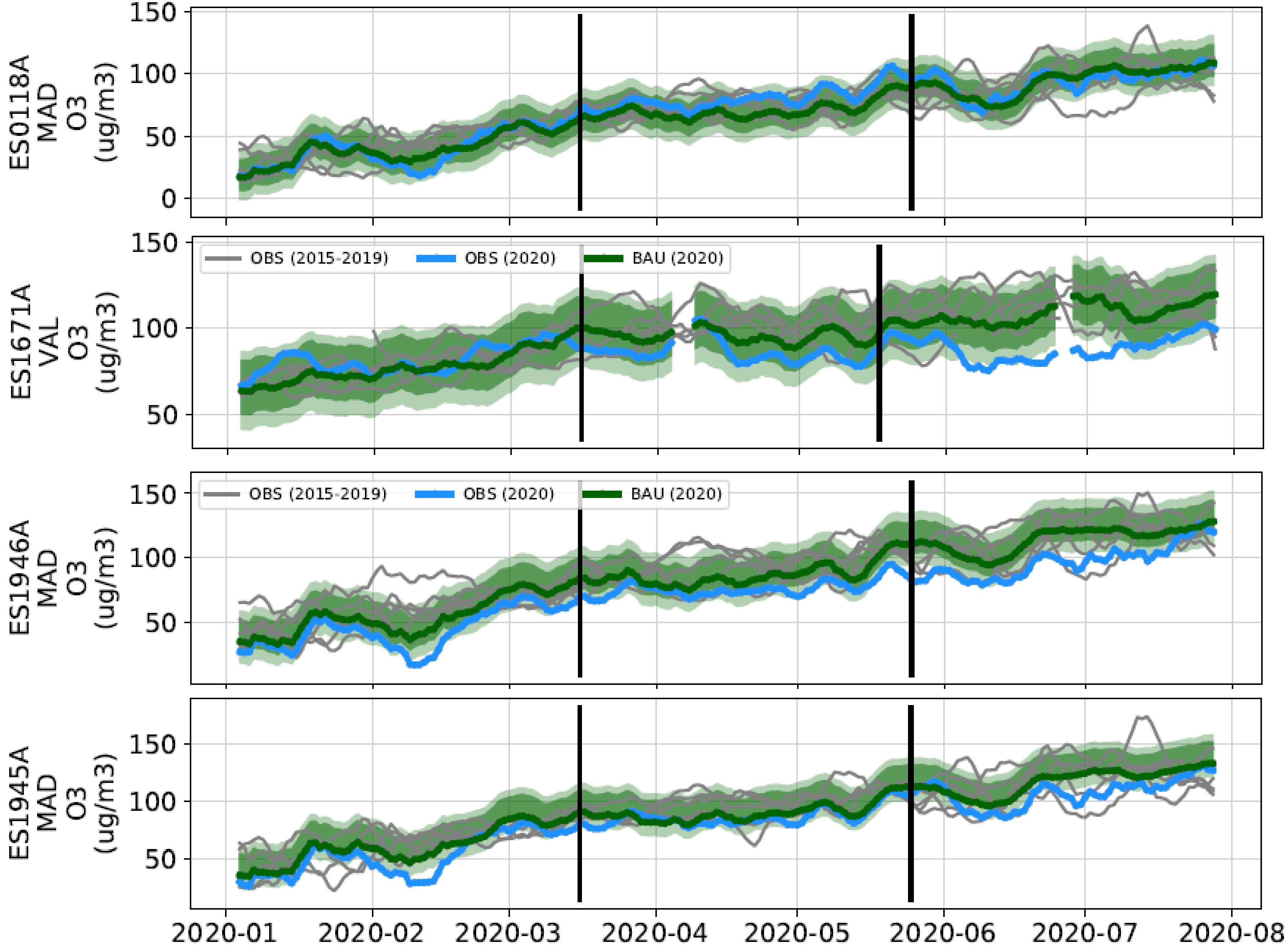
Querol X., et al., 2021. Sci Total Environ.

Results (Time Series 2020)



Querol X., et al., 2021. Sci Total Environ.

Results (Time Series 2020)



Traffic site Madrid E. Aguirre

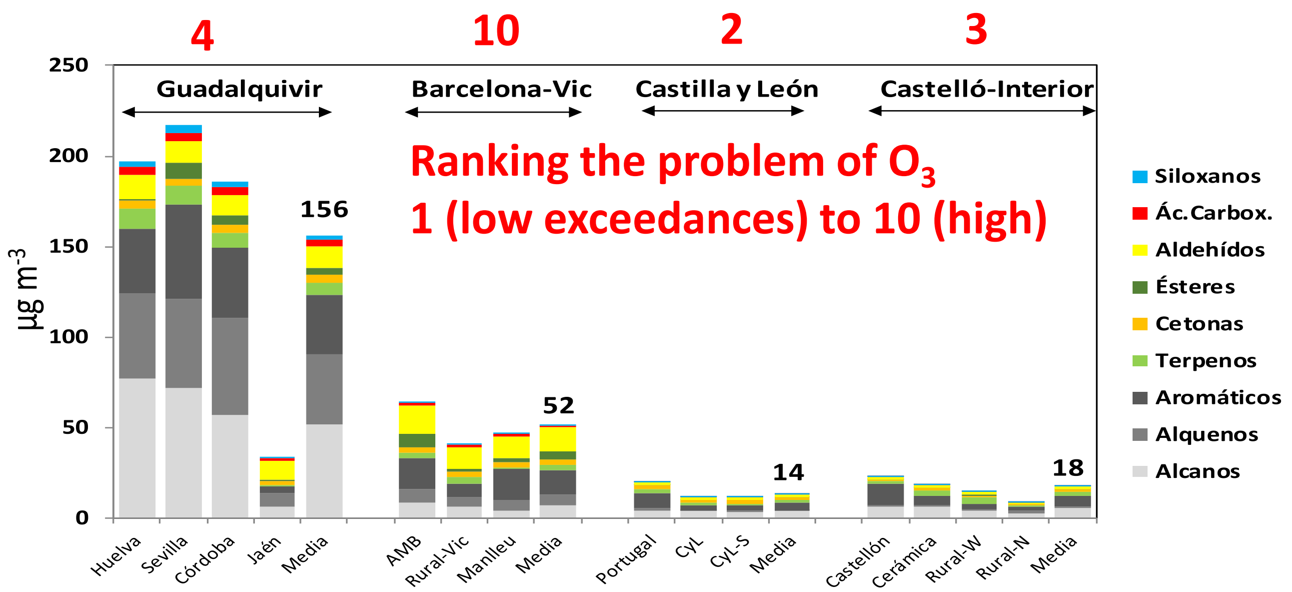
Rural receptor Valencia Villar Arz.

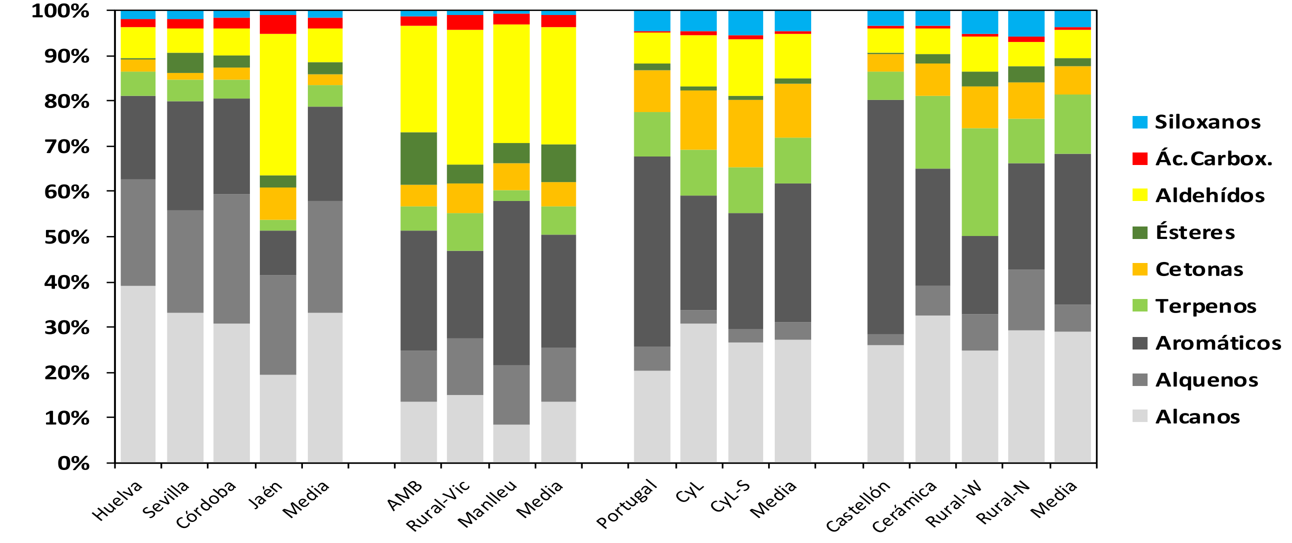
Sub urban receptor Madrid-J.Carlos I

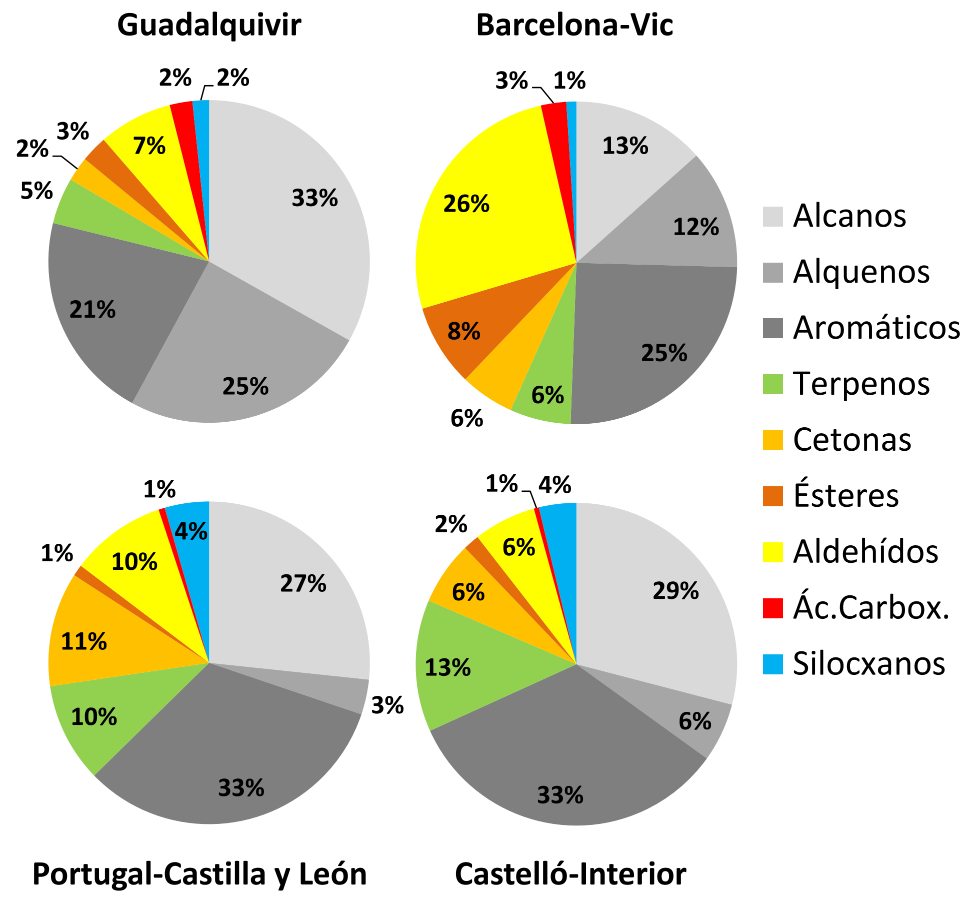
Sub urban receptor Madrid-El Pardo

Querol X., et al., 2021. Sci Total Environ.

Results (VOCs)







Results (VOCs)

Maximum O_3 Formation Potential (MOFP)

TY - JOUR
AU - Carter, William
PY - 2010/01/01
SP - 07
EP - 339
T1 - Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications
VL - 1
JO - California Air Resources Board Contract
ER -

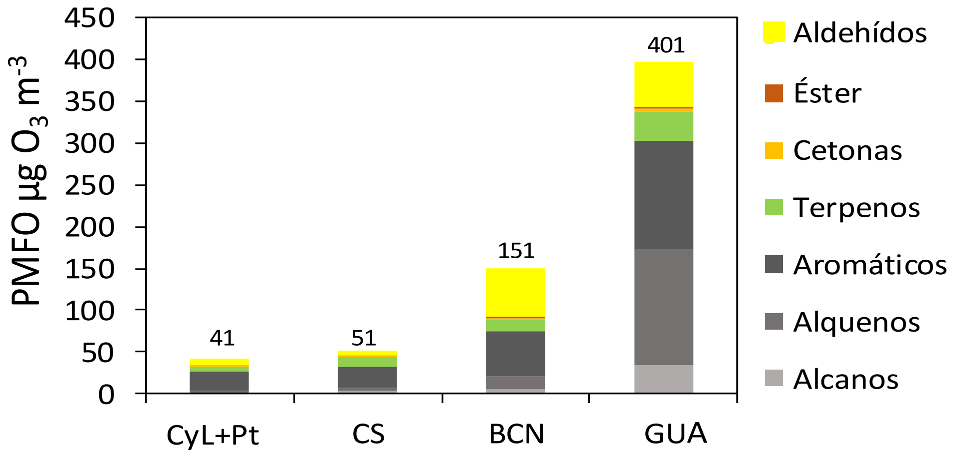
Maximum incremental reactivity (Carter 2009&2010)

$$MIR_i = \frac{\Delta O_3}{\Delta COV_i} \quad (gO_3/gVOC_i)$$

$$MOPF_i = VOC_i * MIR_i \quad (\mu g O_3/m^3)$$

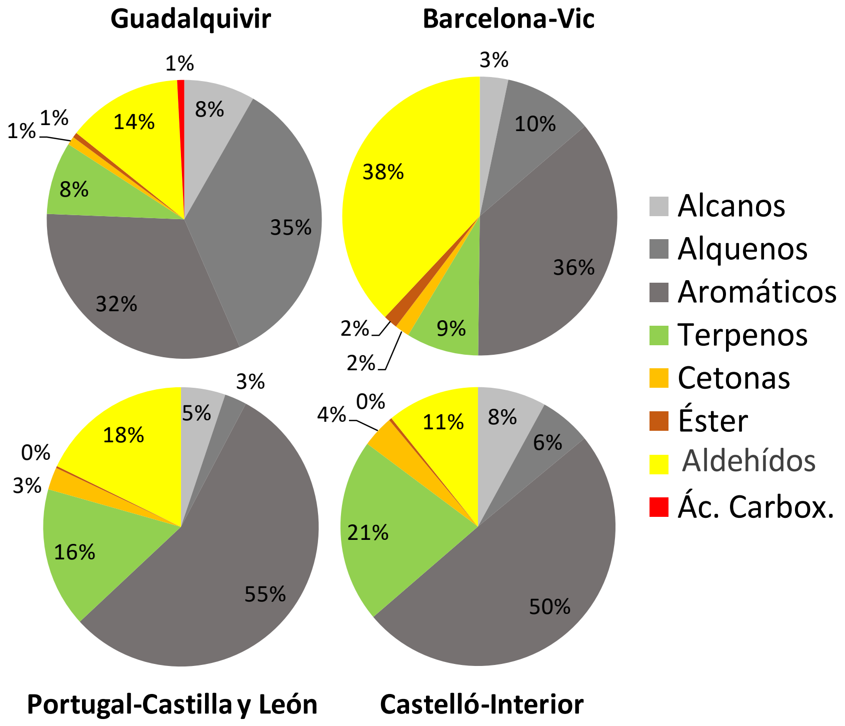
$$MOPF_{TOT} = MOFPa+b+c+\ldots\ldots i$$

Maximum O_3 Formation Potential



2 3 10 4

Ranking of O_3 problem



Results (VOCs)

VOCs with the highest potential for O3 formation depending study basin

GUADALQUIVIR

Alkenes	heptene 100 µg O_3 m^{-3} octene 41 µg O_3 m^{-3}
Aromatic Hy.	Toluene 40 µg O_3 m^{-3}, 1,3,5,-trimetylbenzene 21 µg O_3 m^{-3}, o- & m,p-xylene 17 & 14 µg O_3 m^{-3}
Terpenes	camphene & a-pinene 16 & 11 µg O_3 m^{-3}
Aldehyde	butaldehyde 10 µg O_3 m^{-3}
Alkanes	decane & dodecane 5 & 9 µg O_3 m^{-3}

CASTELLÓ (very similar PORTO-CASTILLA Y LEÓN)

Aromatic Hy.	o,m,p-xylenes & toluene 17 µg O_3 m^{-3} together, etylbenzene, trimetylbenzene 4 µg O_3 m^{-3} together
Terpenes	camphene & m-cymene 6 µg O_3 m^{-3} β-pinene µg O_3 m^{-3}
Alkenes	octene 3 µg O_3 m^{-3}
Alkanes	dimetylbutane (3 µg O_3 $m^{.3}$)
Aldehydes	formaldehyde & butiraldehyde 4 µg O_3 m^{-3} together
Ketones	sabinketona 2 µg O_3 m^{-3}

BCN

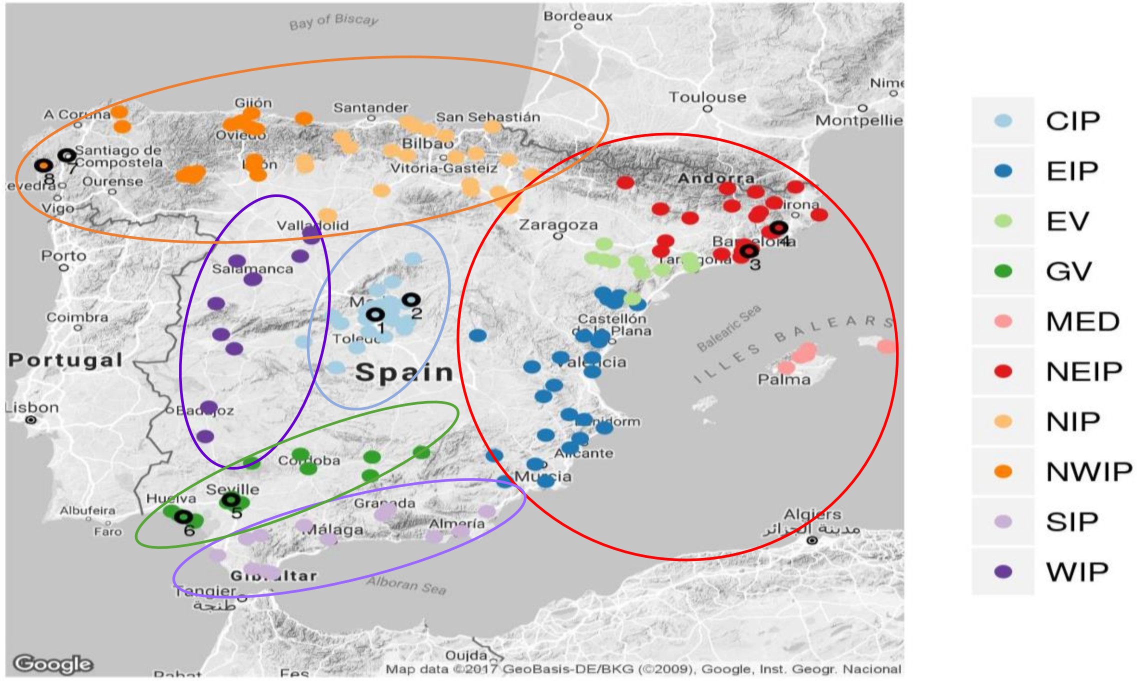
Aromatic Hy.	toluene 21 µg O_3 m^{-3} m,p- & o-xylene 9 & 8 µg O_3 m^{-3} 1,3,5 trimetylbenzene 5 µg O_3 m^{-3}
Alkenes	heptene 11 µg O_3 m^{-3} octene 5 µg O_3 m^{-3}
Aldehydes	heptanal 10 µg O_3 m^{-3} formaldehyde 8 µg O_3 m^{-3} butanal 8 µg O_3 m^{-3} glycolaldehyde 7 µg O_3 m^{-3} pivaldehyde 7 µg O_3 m^{-3} nonanal 5 µg O_3 m^{-3}
Terpenes	a-pinene 6, µg O_3 m^{-3} camphene 6 µg O_3 m^{-3}

Final considerations

1. Complex phenomenology of O_3 pollution episodes known since 1980s
2. 2000-2019 trends are very different to those of 2010-2019
3. Specific regions in Madrid , Valencia, Galicia and Asturias tend to increase O3 for specific parameters and environments
4. VOCs potentially causing high O_3 because high concentrations combined with high MIR should be detected and emissions abated
5. Abatement of emissions due to COVID lockdown reduced O_3 in the O_3 season, when traffic was still reduced by 20-25%
6. WHO AQG O_3 is not attainable, even with the BAT implemented
7. 120 8hDMA target value is exceeded in wide areas and National-EU and Hemispheric measures are required for meeting the standard
8. Local-regional-National measures shall be implemented to abate emissions in 4 major basins where acute pollution of O_3 is recorded
9. The concept of critical loads for air pollution is relevant
10. Measures should be specially implemented in May-July

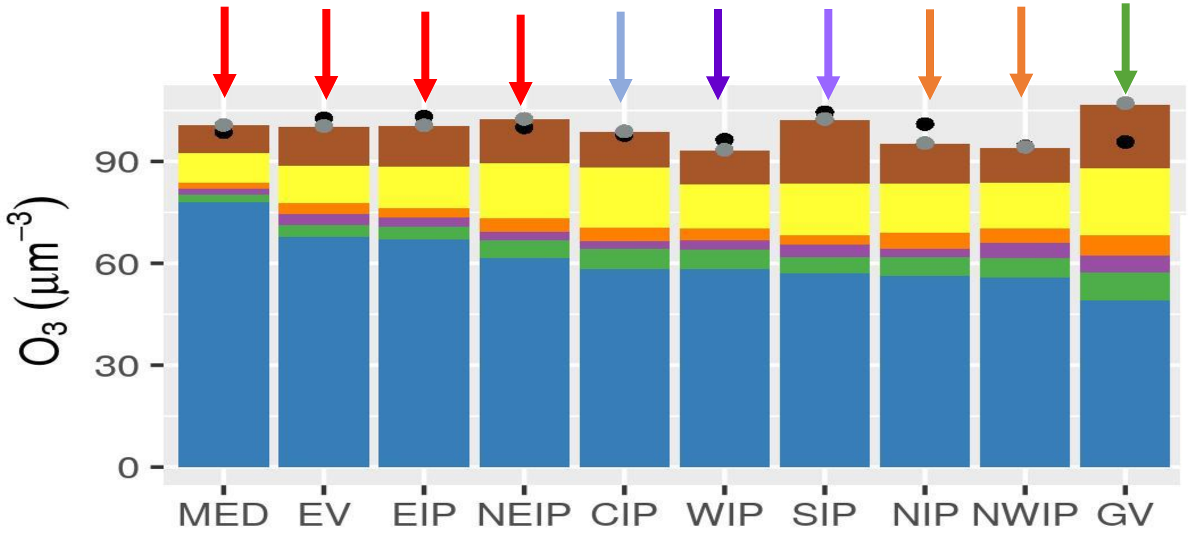
Examples of the expected results for source apportionment (before sensitivity A.)

Regionalization of source-sector contribution



Pay et al. (2019,ACP)

Daily mean contribution during DMA8 > 120 μ/m³



r =0.79 (without GV)

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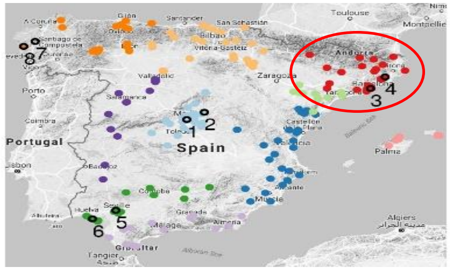
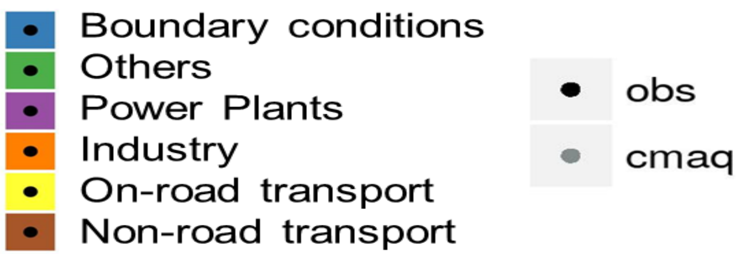
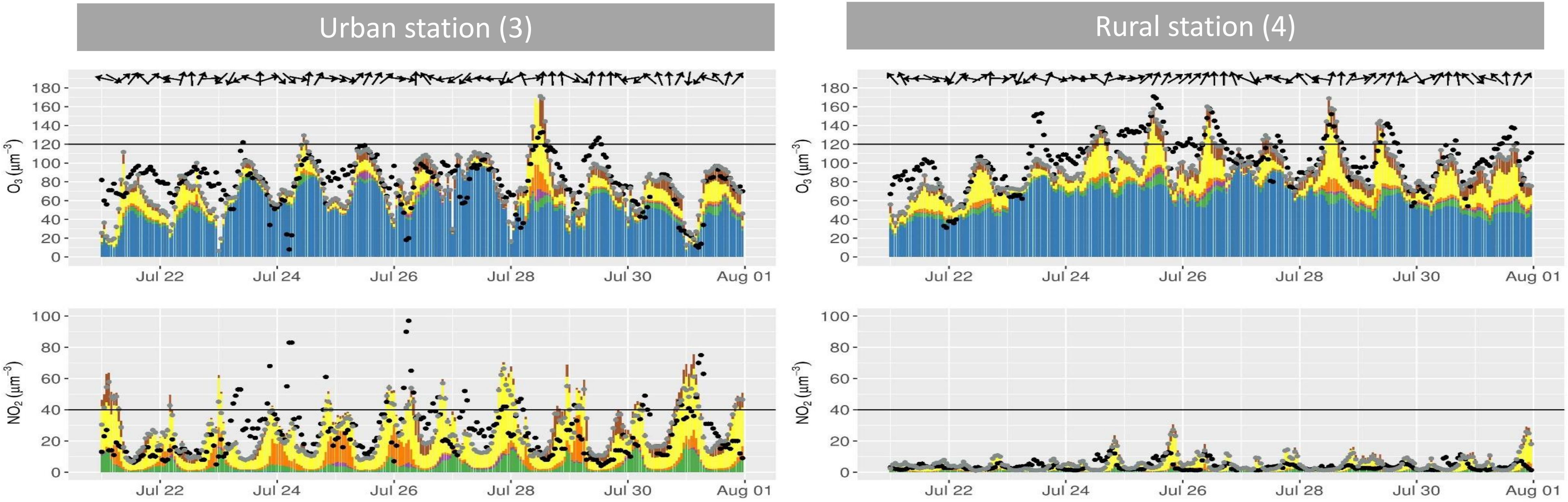
Centro Nacional de Supercomputación

Examples of the expected results for source apportionment (before sensitivity A.)

Northeastern Iberian Peninsula (NEIP)







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Thank you for your attention!!!!!

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