

2n Congrés
**Qualitat
de l'**



14-15 d'octubre 2021

**#CongresAire
#AireNet**

SESIÓN: Ozono troposférico, episodios, precursores y comportamiento durante el confinamiento COVID19

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Moderat per:

XXXXXX, nom d l'organització.

Xavier Querol, Instituto de Diagnóstico Ambiental y Estudios del Agua, IDAEA-CSIC



O_3 PLAN TEAM

***X. Querol¹, A. Alastuey¹, J. Massagué¹, C. Carnerero¹, N. Pérez¹, M. in 't Veld¹,
M.T. Pay², H. Petetin², M. Guevara², O. Jorba², C. Pérez García-Pando²,
G. Gangoiti³,
E.Mantilla⁴, J.J.Diéguez⁴, A. Muñoz⁴, E. Borrás⁴, T. Vera⁴, M.Millán⁴,
M.Escudero⁵,
E. Monfort⁶, I. Celades⁶, V. Sanfelix⁶, A. López-Lilao⁶,
J. de la Rosa⁷, A. Sánchez de la Campa⁷,
C. Alves⁸***

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

²Department Earth Sciences, Barcelona Supercomputing Centre (BSC), Barcelona, Spain

³E.T.S. Ingeniería de Bilbao, Dpto. Ingeniería Química y del Medio Ambiente, Universidad País Vasco UPV/EHU, Bilbao, Spain

⁴Centro de Estudios Ambientales del Mediterráneo, CEAM, Unidad Asociada al CSIC, Valencia, Spain

⁵Centro Universitario de la Defensa de Zaragoza, Academia General Militar, Zaragoza, Spain

⁶Instituto de Tecnología Cerámica, Universitat Jaume I (ITC-UJI), Castelló, Spain

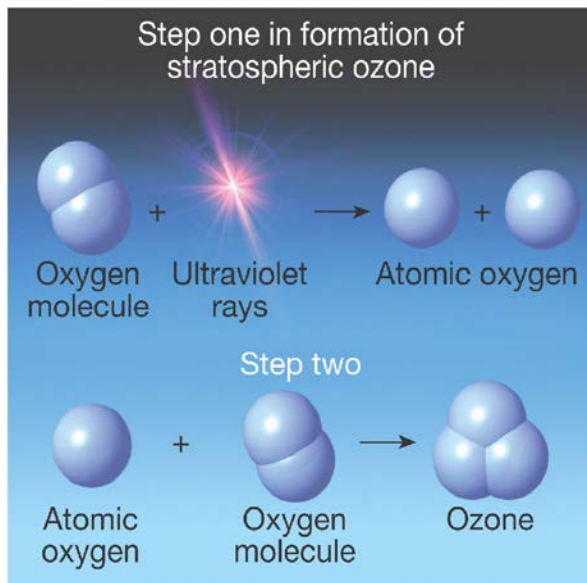
⁷Departamento de Ciencia de la Tierra, Universidad de Huelva (UHU), Spain

⁸Universidade de Aveiro (UA), Portugal

OUTLINE

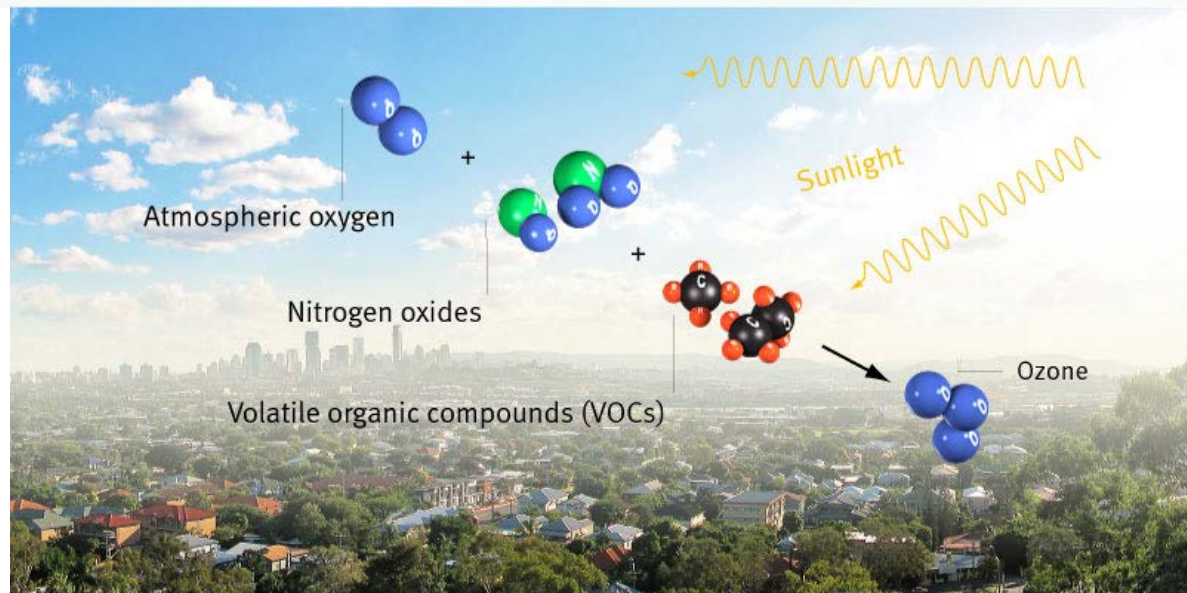
- O_3 in the atmosphere
- Levels of O_3 in Spain
- Phenomenology of O_3 episodes in Spain
- VOCs Precursors in Spain
- O_3 and COVID19 pandemic

O_3 in the stratosphere



<http://www.geo.hunter.cuny.edu>

O_3 in the troposphere

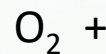
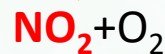
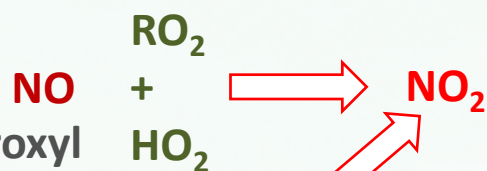
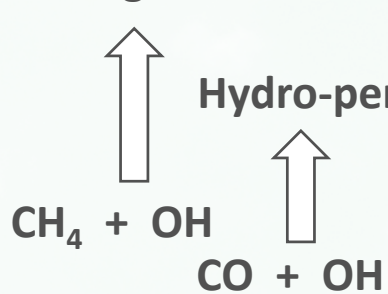


<https://www.qld.gov.au/environment/pollution/monitoring/air-pollution/ozone/>

Queensland State Government, Australia

- Alkanes
- Alkenes
- Carbonyls (aldehydes & ketones)
- PAHs
- Alcohols
- Organic peroxides
- Halogenated VOCs

Organic radicals

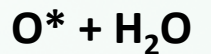
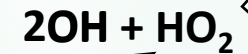
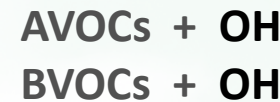


How O_3 is consumed?

$NO + O_3$
in urban areas
 O_3 is consumed

- Isoprene 1h
- Methane 10 yr

Photolysis of aldehydes in polluted areas HONO & H₂O₂



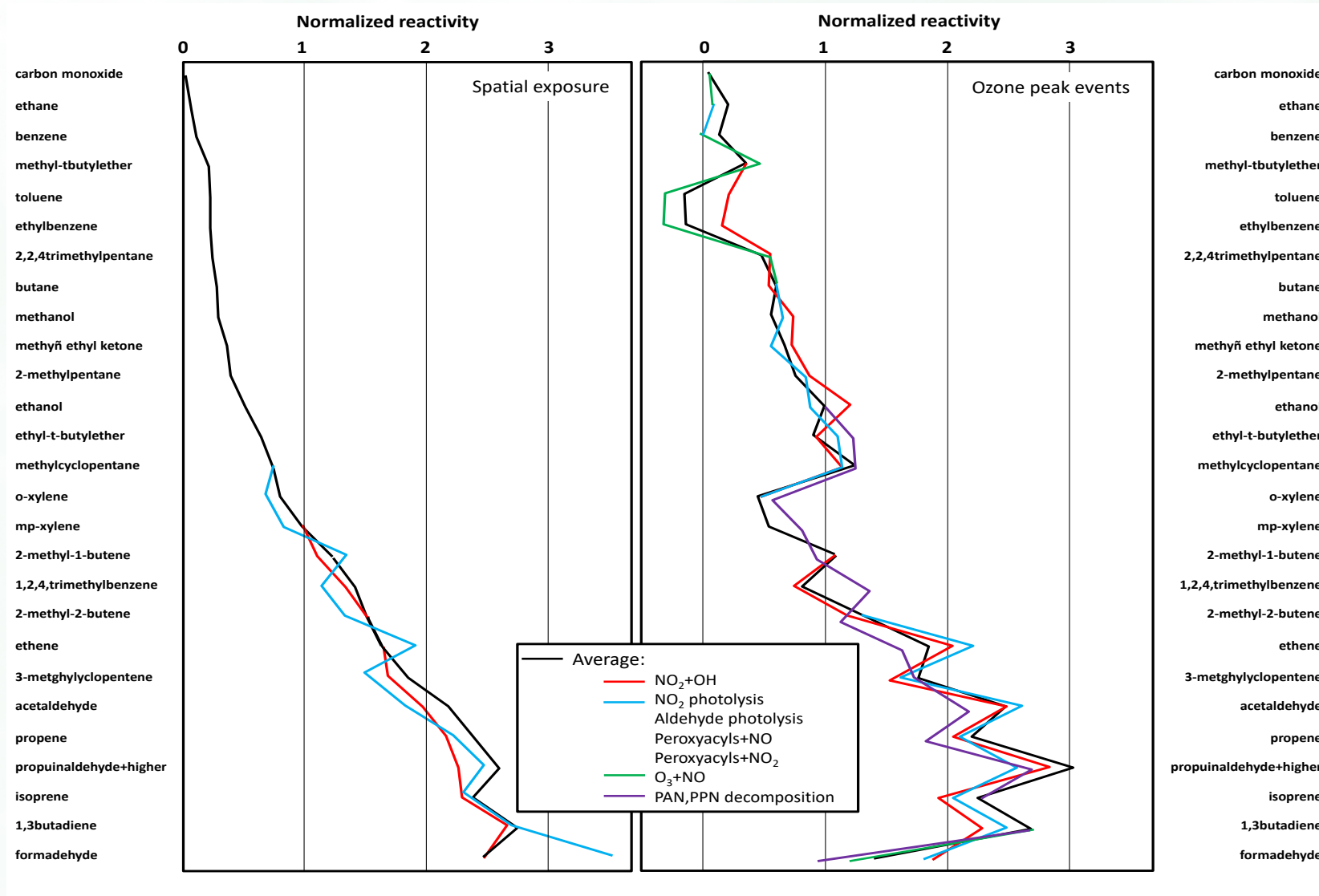
Reaction with vegetation:

- Stomatal deposition
- Non-stomatal deposition

Deposition in water

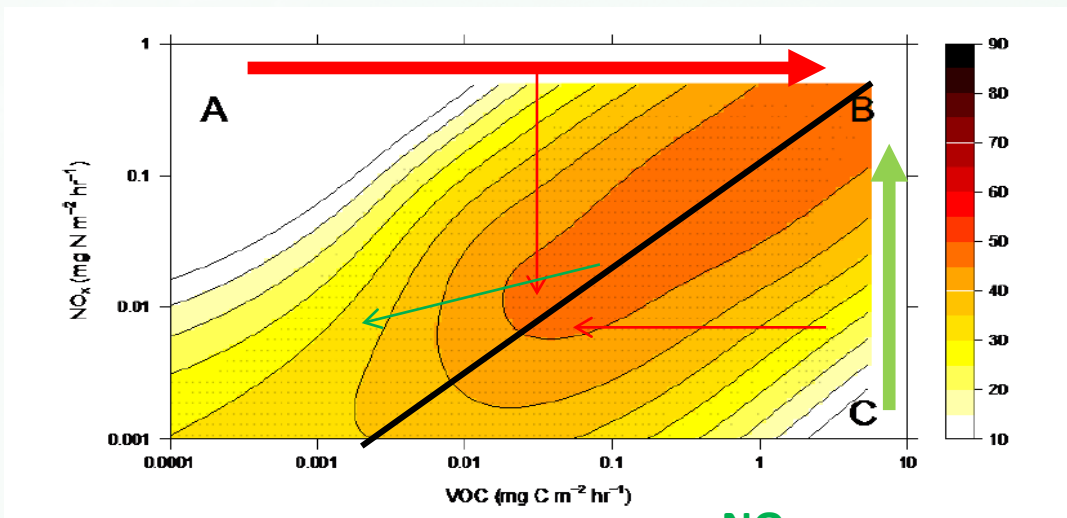
O₃ IN THE ATMOSPHERE

VOCs reactivity for O₃ formation



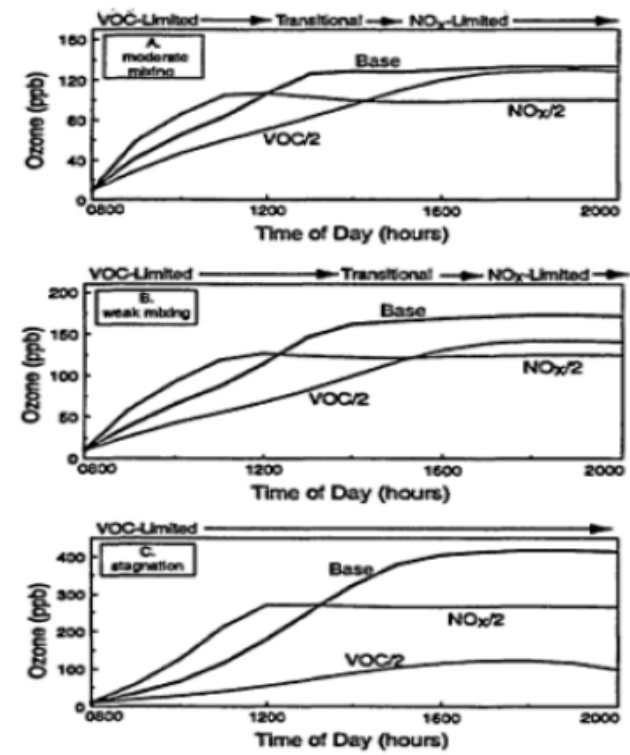
O₃ IN THE ATMOSPHERE

VOCs limited $\text{OH} < \text{NO}_x$



Monks et al., 2015, ACP

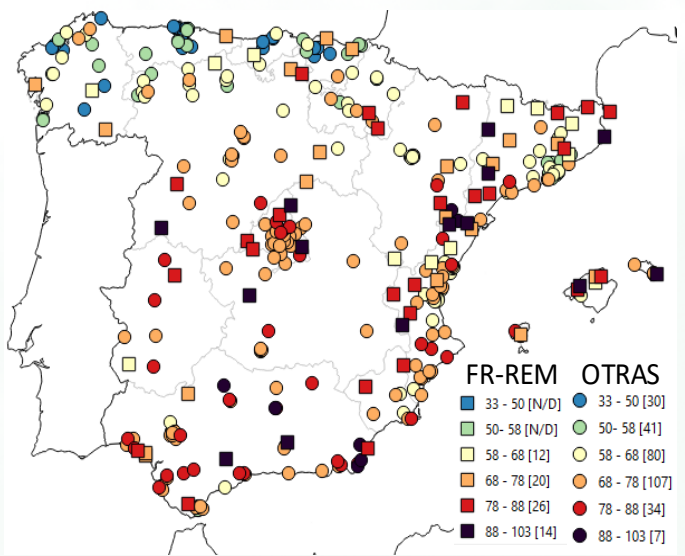
NO_x
 $\text{OH} > \text{NO}_x$



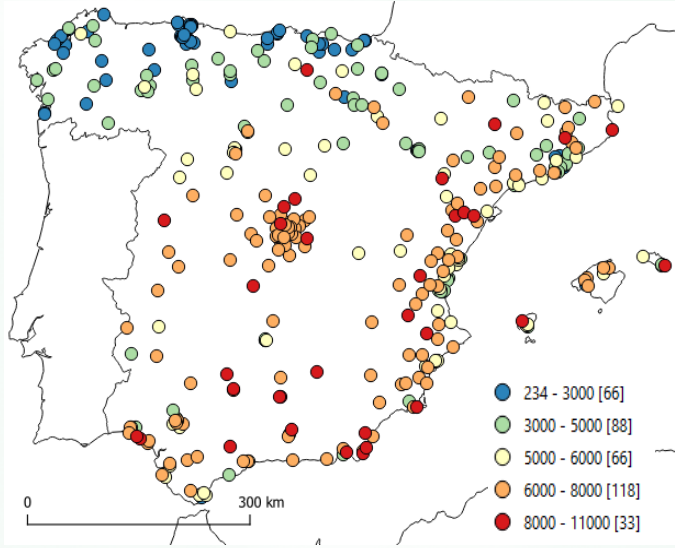
Bergin M.S. et al., 1998. Environ. Sci. Technol. 32 (5), 694-703

LEVELS OF O₃ IN SPAIN

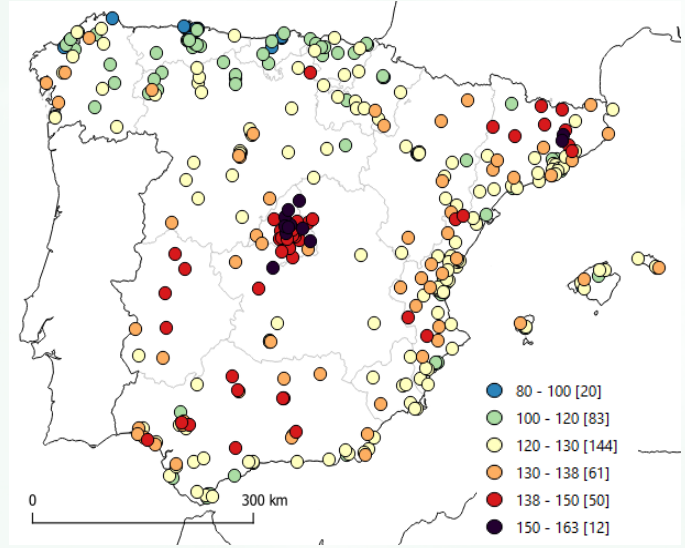
Media O₃ Abr-Sep ($\mu\text{g m}^{-3}$)



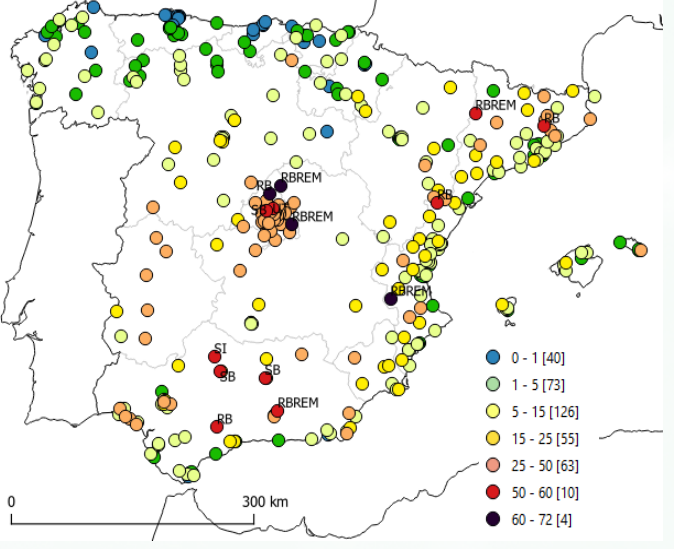
SOMO35 ($\mu\text{g m}^{-3}$ día)



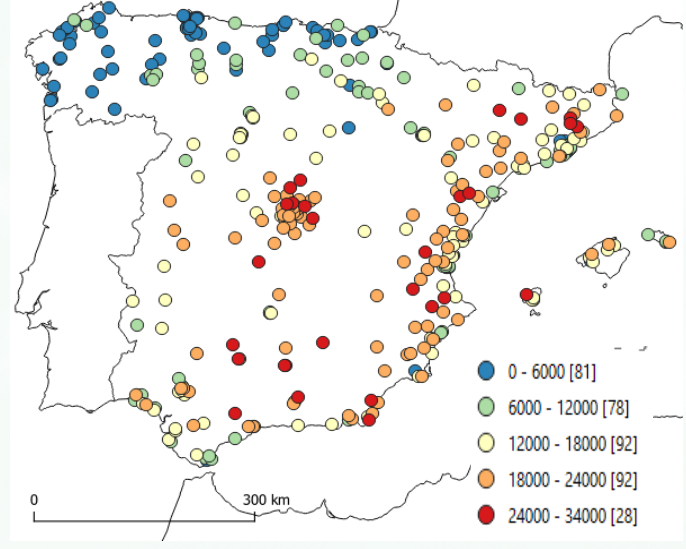
P98 MD8h ($\mu\text{g m}^{-3}$)



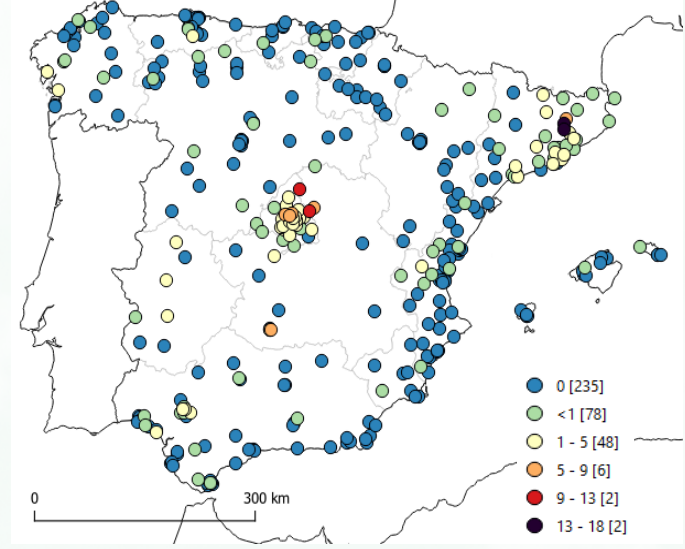
> 120 $\mu\text{g m}^{-3}$ MD8h año⁻¹



AOT40 VEG ($\mu\text{g m}^{-3}$ h)



> 180 $\mu\text{g m}^{-3}$ (h año⁻¹)



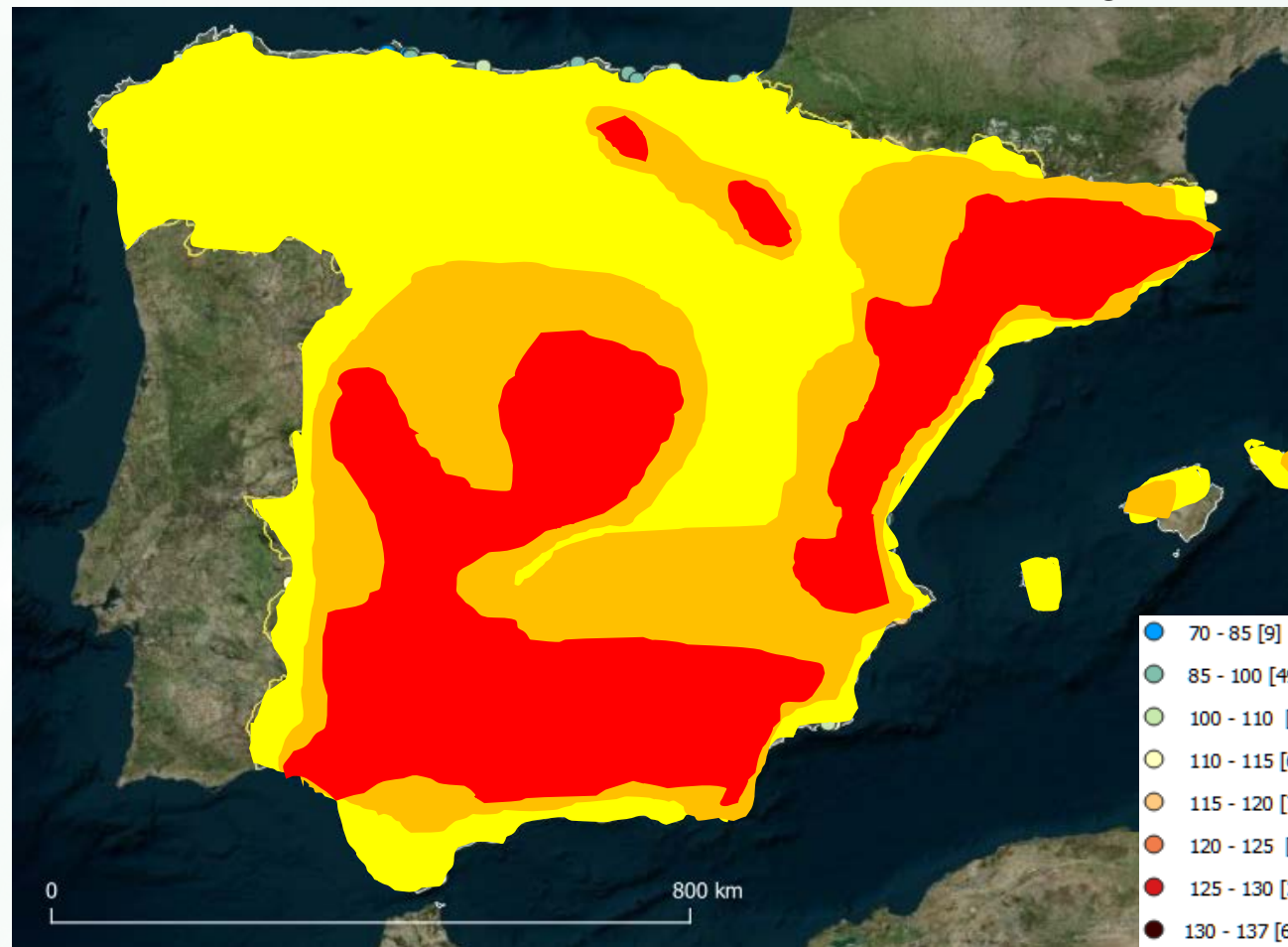
LEVELS OF O₃ IN SPAIN

Averages 2010-2019

Exceedance of the EU AQ Health protection target value Close to EU AQ target value

Exceedance of the WHOAQG

Averaged 93.2 percentile 8h-DM O₃



TYPE 1 O₃ REGIONS

TYPE 2 O₃ REGIONS

TYPE 3 O₃ REGIONS

LEVELS OF O₃ IN SPAIN

Averages 2010-2019

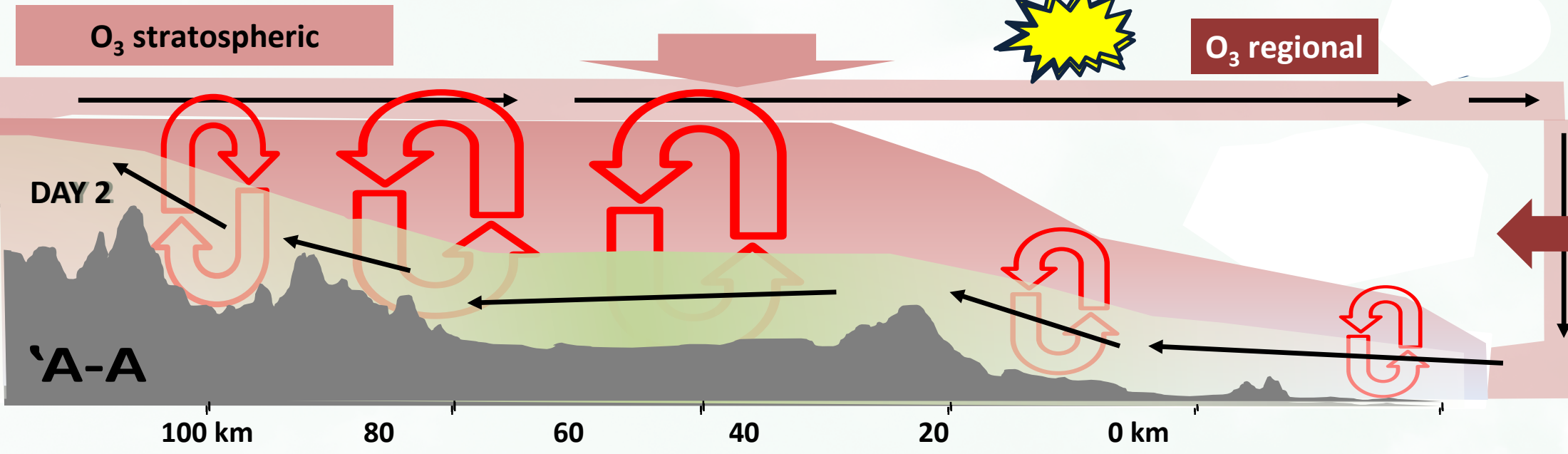
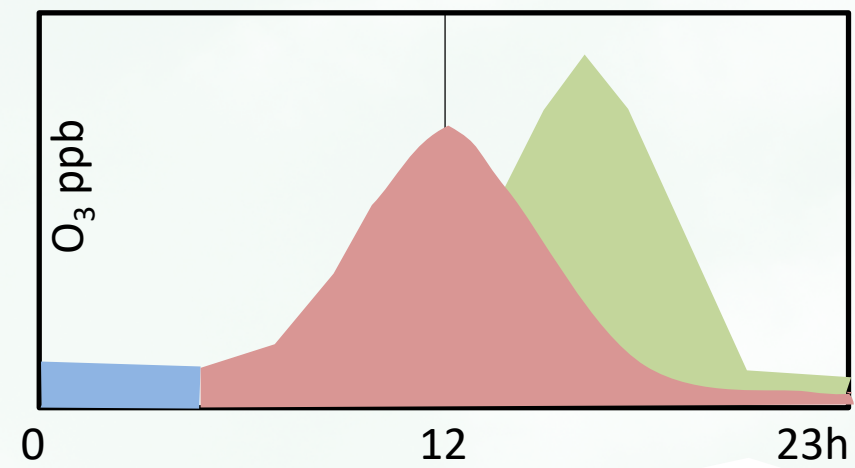
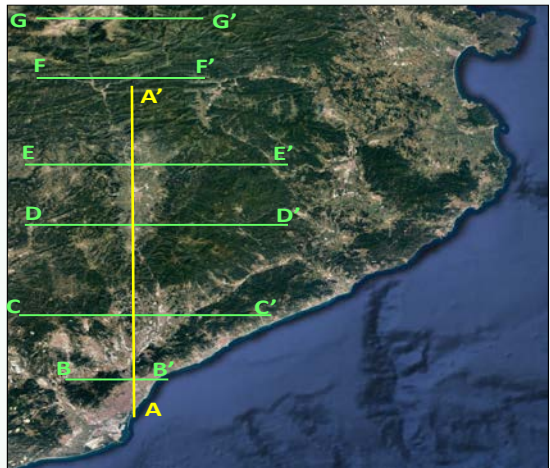
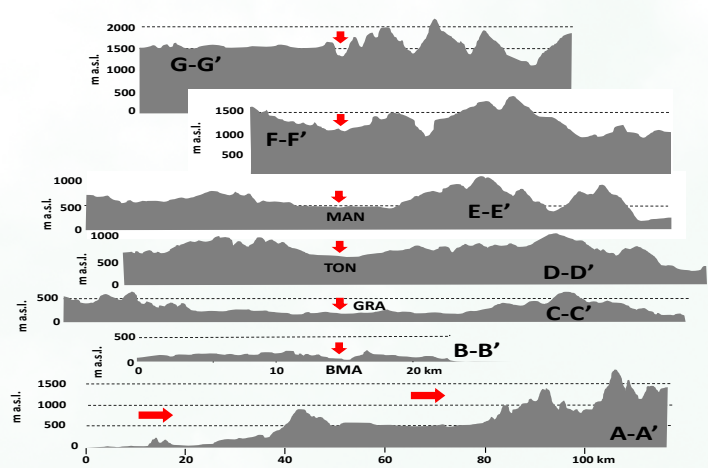
Daily exceedances >180 µg m⁻³



TYPE 3 O₃ REGIONS

PHENOMENOLOGY OF O₃ EPISODES

TYPE 3 O₃ REGIONS: NORTH OF BARCELONA

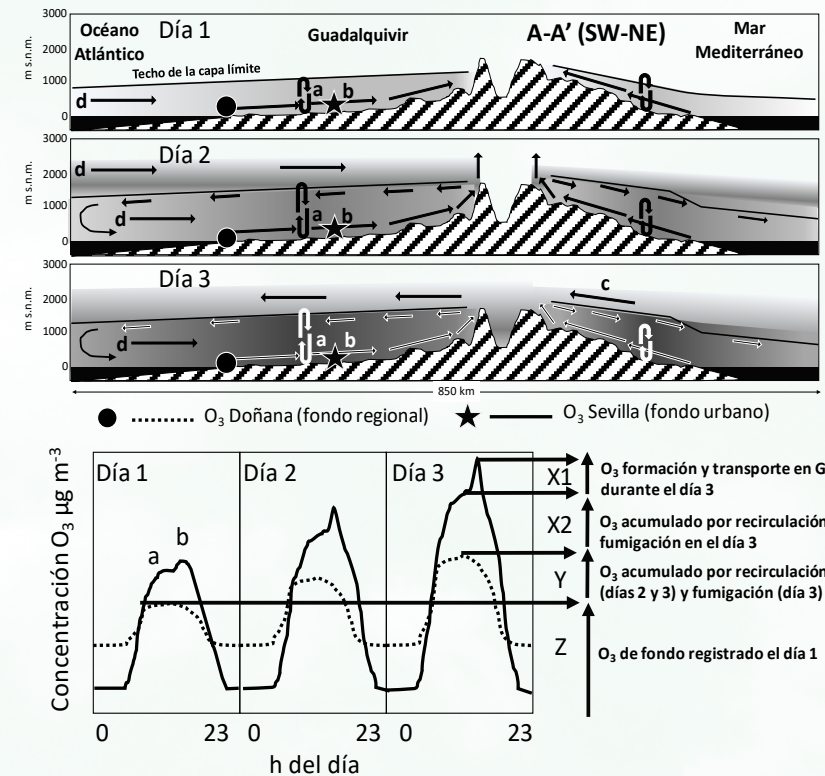
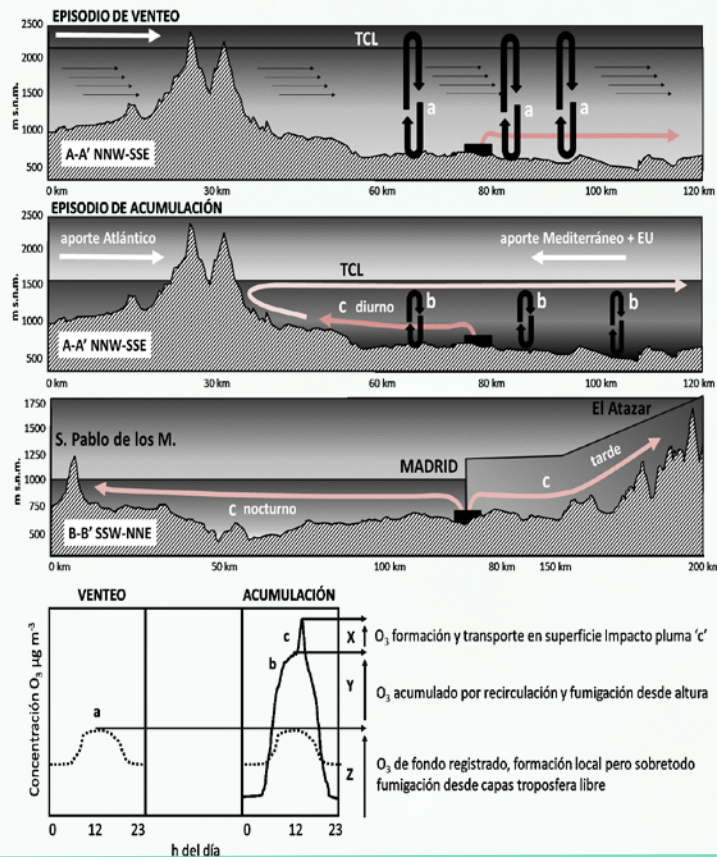




- MADRID
- GUADALQUIVIR



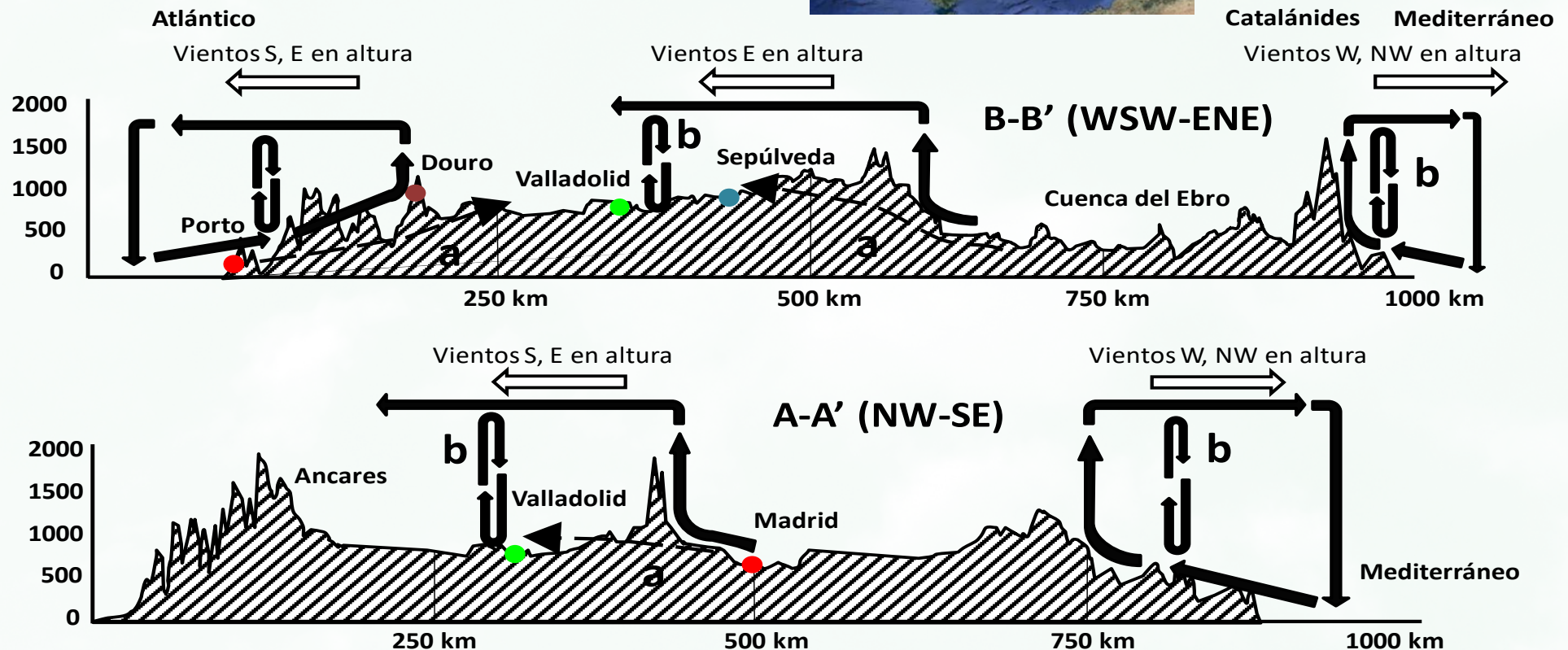
- a) Recirculación vertical y fumigación
- b) Formación local y transporte en el valle
- c) Transporte en altura des del Mediterráneo afectado por fumigación
- d) Transporte desde Atlántico



PHENOMENOLOGY OF O₃ EPISODES

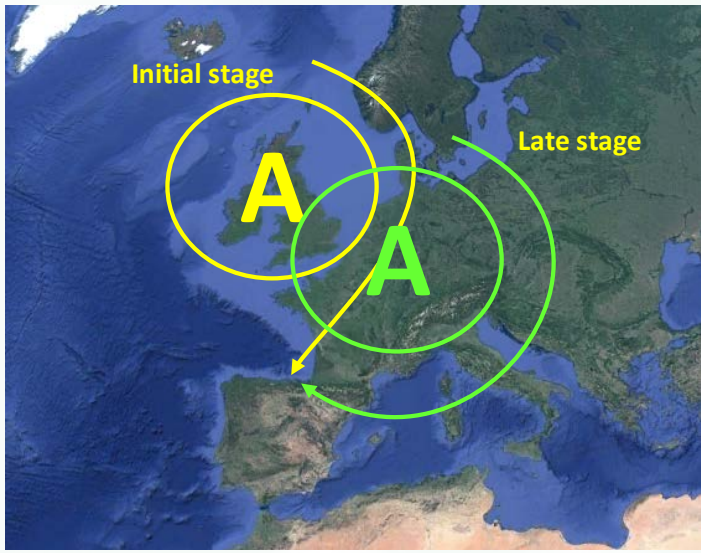
TYPE 2 O₃ REGIONS: CASTILLA Y LEÓN

- a. Transporte por superficie
- b. Transporte en altura y fumigación desde allí

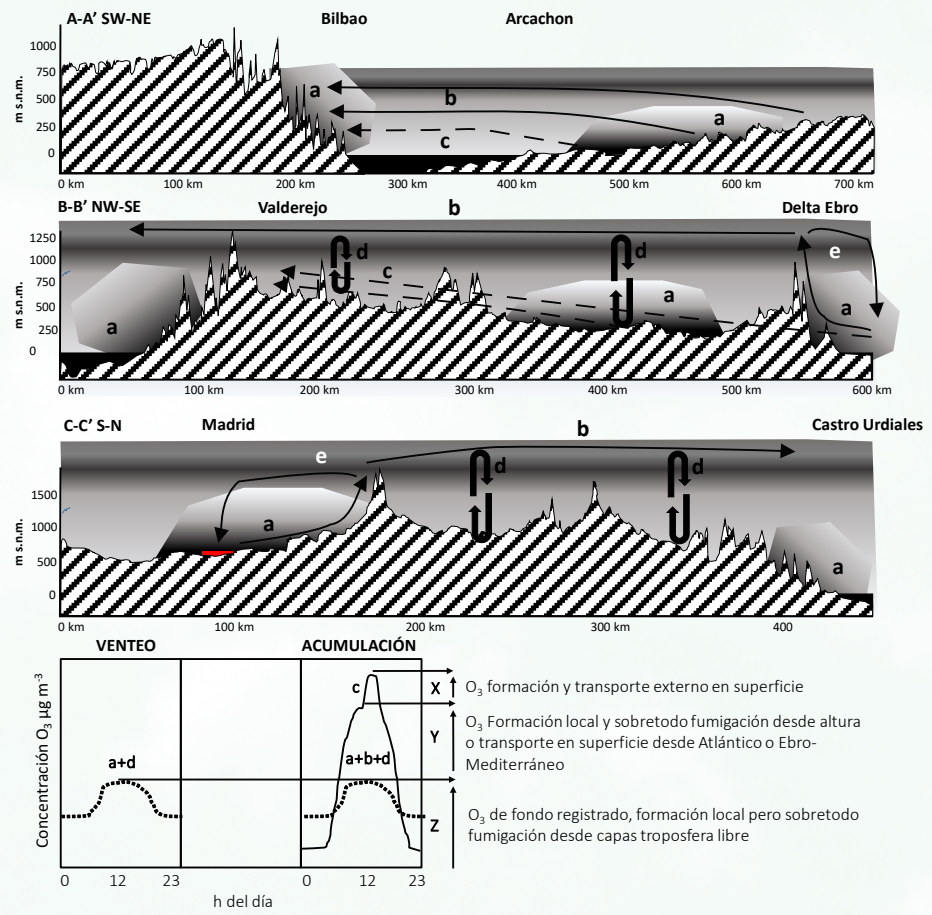


PHENOMENOLOGY OF O₃ EPISODES

TYPE 1 O₃ REGIONS: EUSKADI

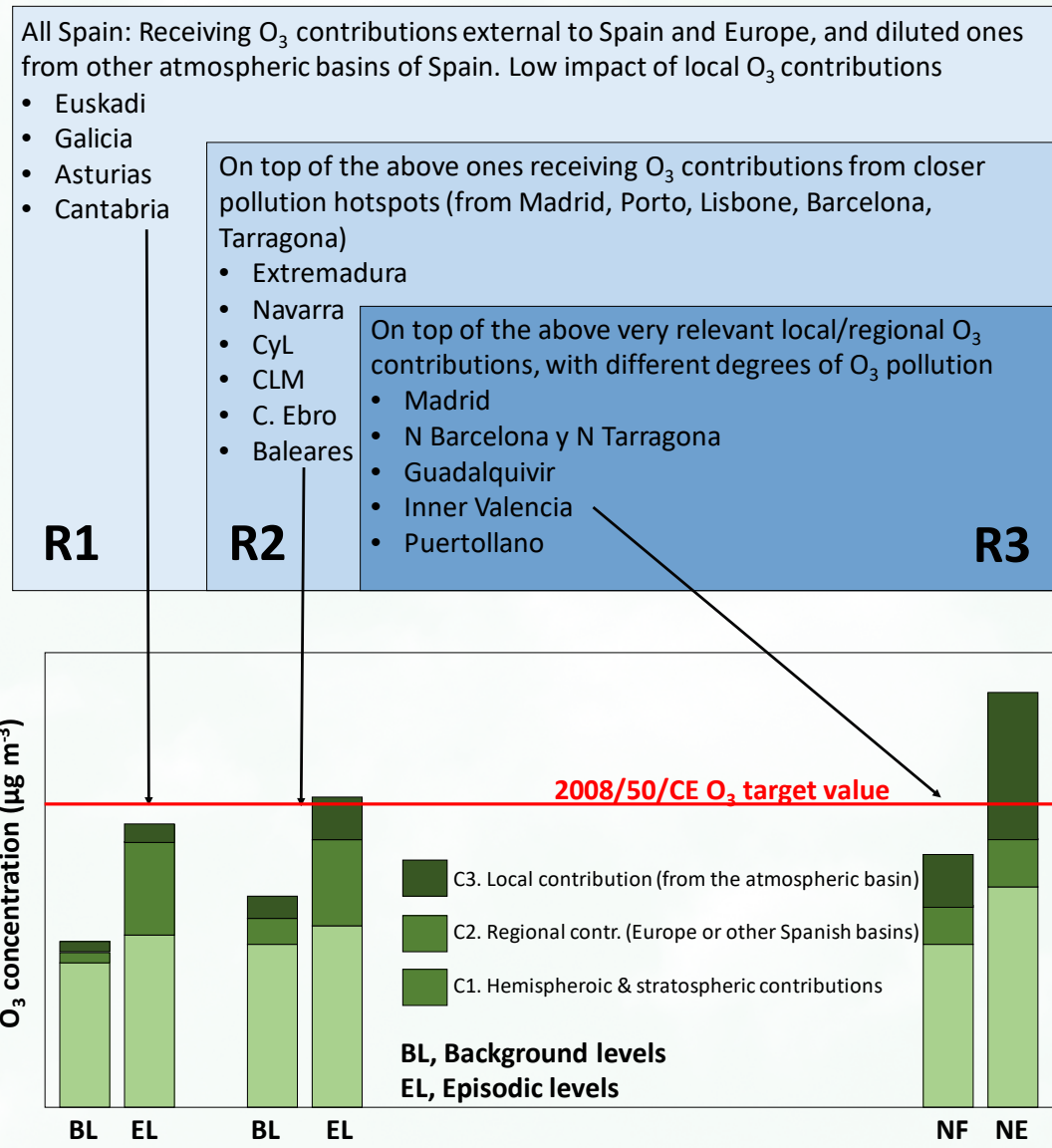


- a. Generación local/regional de O₃
- b. Inyección y transporte de O₃ en altura
- c. Transporte de O₃ en superficie
- d. Fumigación desde capas altas
- e. Recirculación vertical de masas de aire



PHENOMENOLOGY OF O₃ EPISODES

A POSSIBLE STRATEGY FOR A SPANISH O₃ PLAN



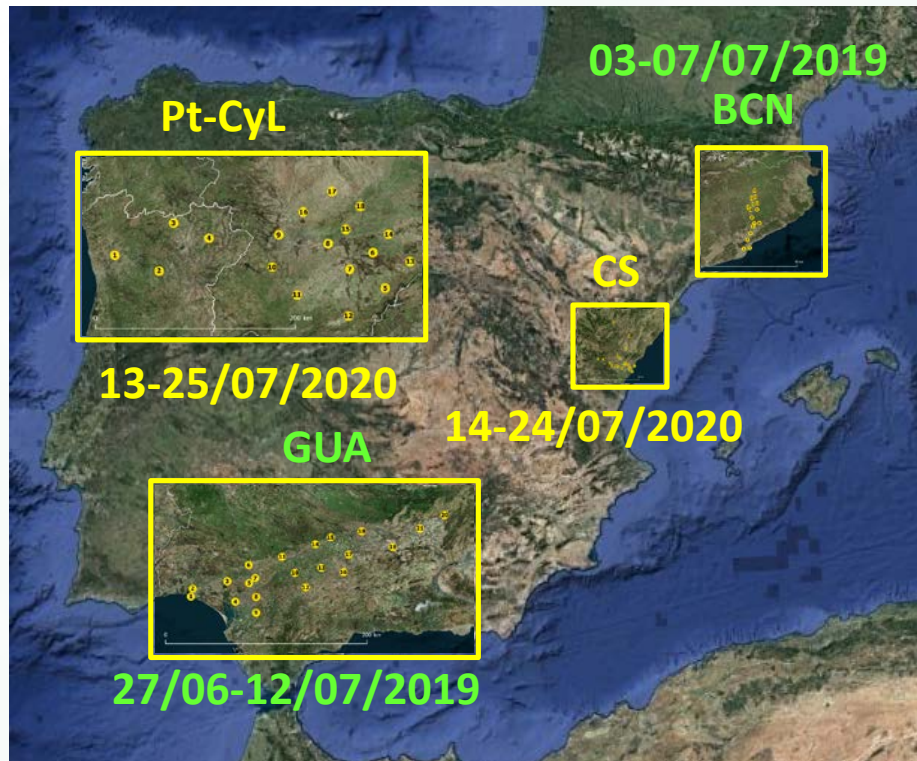
PHENOMENOLOGY OF O₃ EPISODES

THE HIGHEST O₃ AQ MONITORING SITE IN EACH AUTONOMOUS REGION 2025-2019

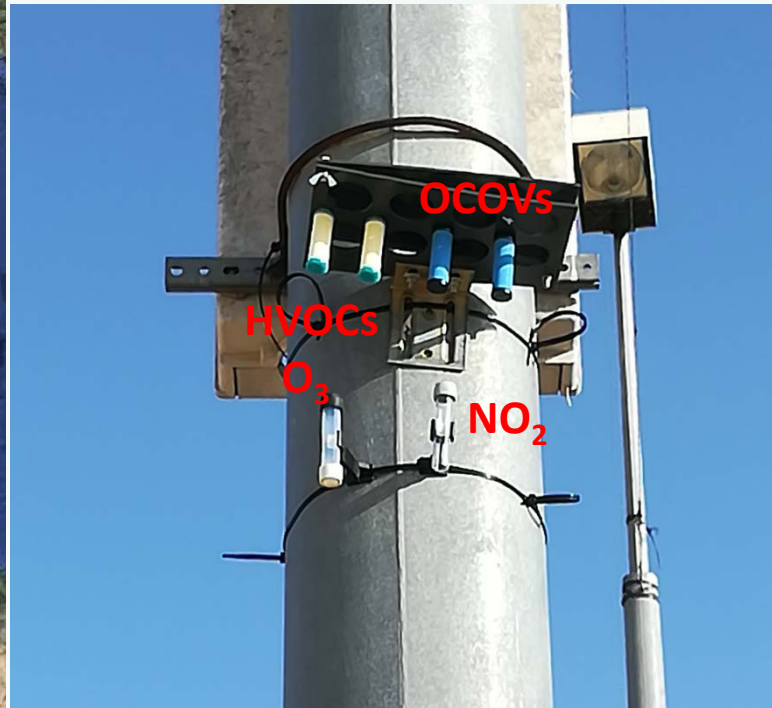
Autonomous regions	O ₃ Apr.-Sep. (µg m ⁻³)	O ₃ peak season (µg m ⁻³)	AOT40 veg. (µg m ⁻³ hour)	SOMO35 (µg m ⁻³ day)	Exc. TVHP (day yr ⁻¹)	p93.2 (µg m ⁻³)	4th highest 8hDM (µg m ⁻³)	Exc. Info. Tresh. (hours yr ⁻¹)
Andalucía	99	115	31633	10776	59	131	145	2.4
Aragón	92	106	22902	8336	26	121	134	0.4
Asturias	75	88	6367	5091	5	106	124	1.0
Islas Baleares	91	104	25110	8648	27	122	133	0.2
Comunidad Valenciana	102	115	33420	10875	64	131	144	1.2
Islas Canarias	75	83	6397	5096	7	105	116	0.2
Cantabria	67	81	5096	4392	3	103	119	0.2
Cataluña	101	111	29800	10434	54	135	161	17.6
Castilla La Mancha	99	111	24332	9664	47	127	153	10.4
Castilla y León	88	106	21964	8537	32	123	138	0.4
Extremadura	84	107	19465	7182	40	125	147	3.6
Galicia	73	87	7626	5191	14	111	136	4.2
Madrid	95	116	27597	10607	72	141	163	9.8
Murcia	84	104	21911	8236	25	119	134	0.3
Navarra	82	101	18902	6677	24	120	136	0
País Vasco	81	102	16151	8034	30	122	140	0.8
La Rioja	73	94	15256	5365	15	114	127	0

O₃ PRECURSORS IN SPAIN

VOCs MEASUREMENT CAMPAIGNS JULY 2019 & 2020



GC-MS



Limitations

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

Pros

- Easily deployed
- Spatial variations

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)

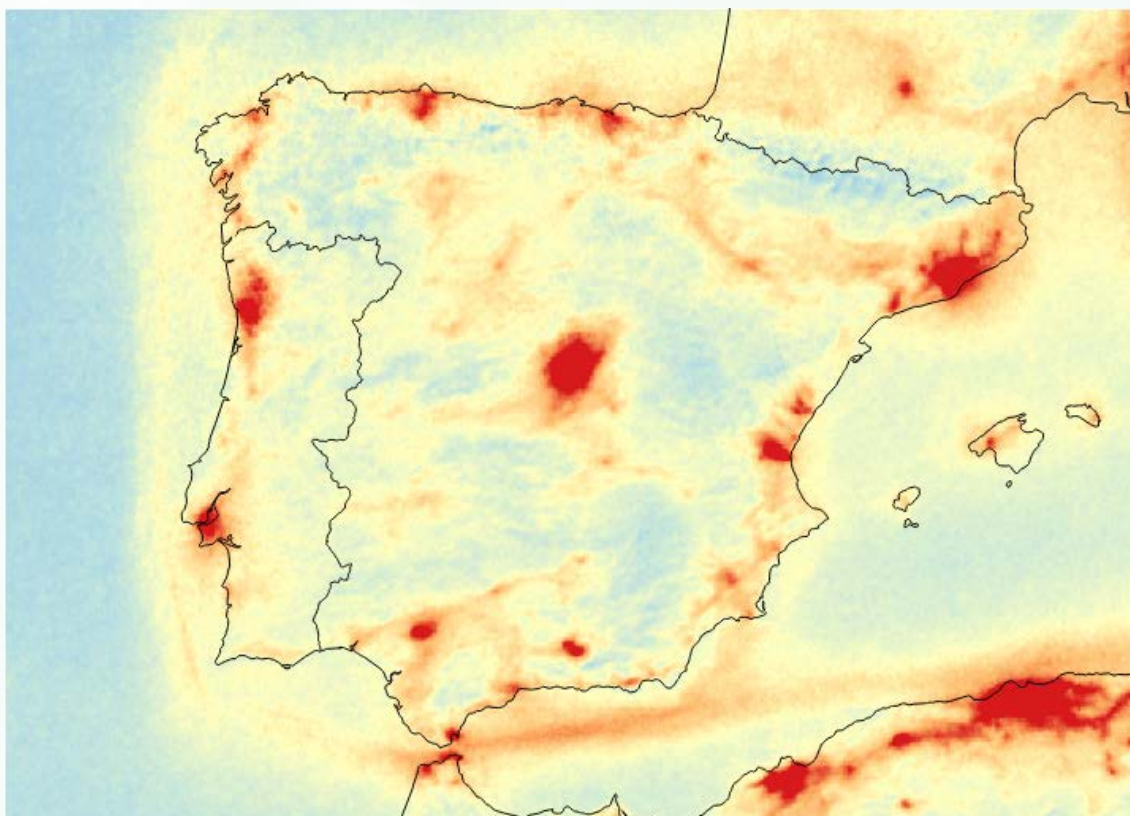
CS 19 sites, 44 VOCs (30 HVOCs y 14 OVOCs)

O₃ PRECURSORS IN SPAIN

TROPOMI –ESA- NO₂ COLUMN JJA 2019

NO₂ ($\mu\text{mol m}^{-2}$)

0 40

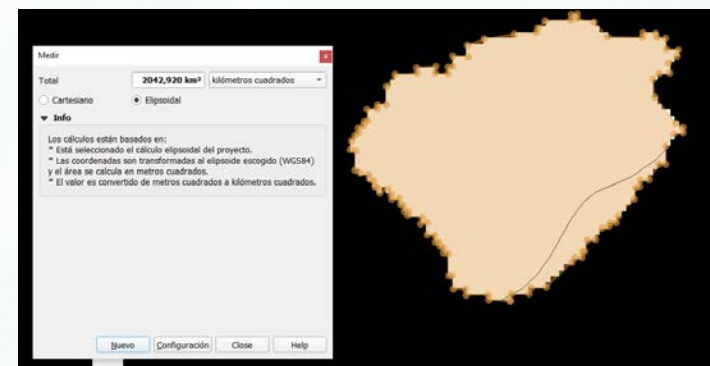


AREA WITH NO₂ $\geq 40 \mu\text{mol m}^{-2}$

Madrid 2733 km² elipsoidal
(4730 km² cartesian)

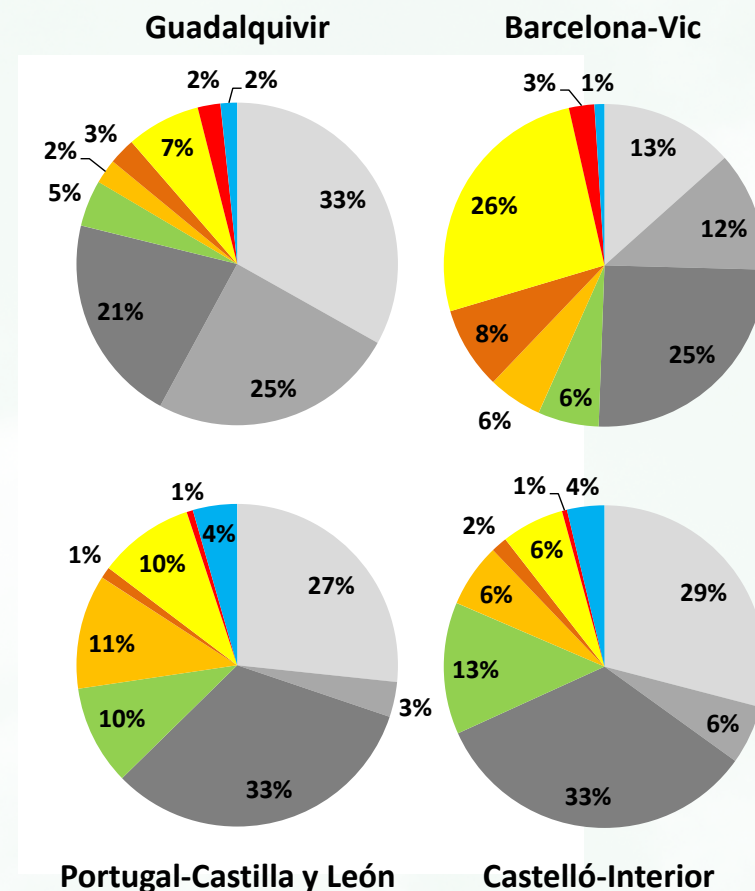
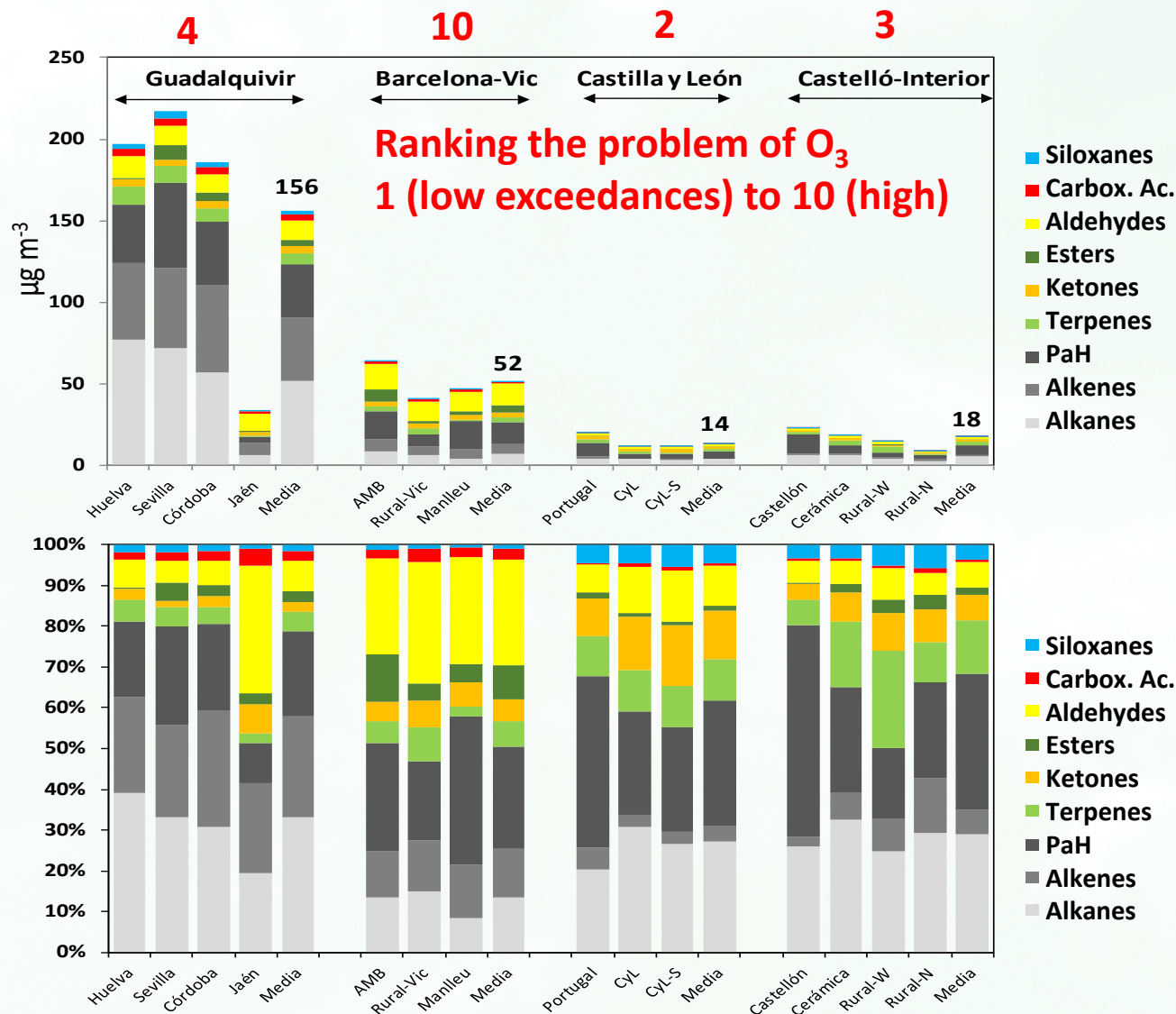


Barcelona 2043 km² elipsoidal
(3649 km² cartesian)



O₃ PRECURSORS IN SPAIN

VOCs MEASUREMENT CAMPAIGNS JULY 2019 & 2020



O₃ PRECURSORS IN SPAIN

VOCs MEASUREMENT CAMPAIGNS JULY 2019 & 2020

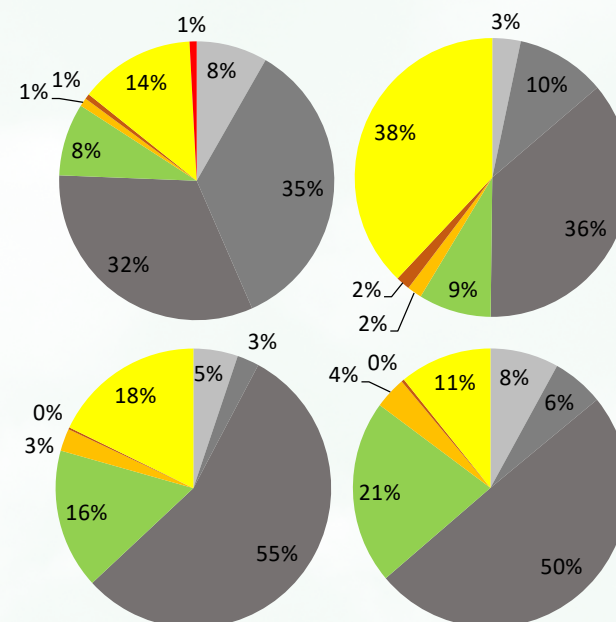
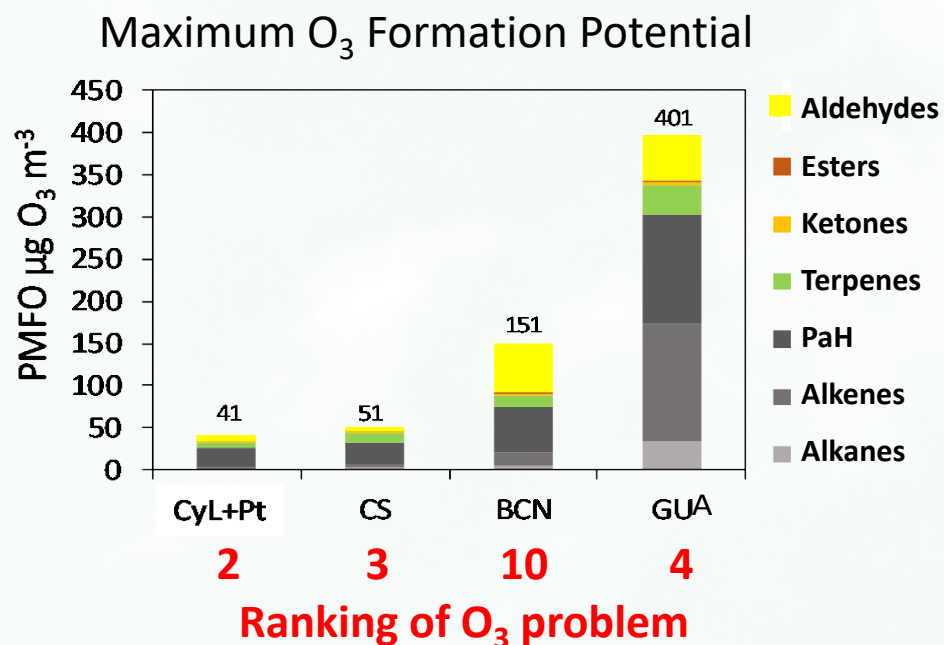
TY - JOUR
AU - Carter, William
PY - 2010/01/01
SP - 07
EP - 339
T1 - Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications
VL - 1
JO - California Air Resources Board Contract
ER -

Maximum O₃ Formation Potential (MOFP)
Maximum incremental reactivity (Carter 2009&2010)

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

$$MOPF_i = VOC_i * MIR_i \quad (\mu gO_3/m^3)$$

$$MOPF_{TOT} = MOPF_a + b + c + \dots + i$$



O₃ PRECURSORS IN SPAIN

GUADALQUIVIR MAXIMUM O₃ FORMATION POTENTIAL BCN

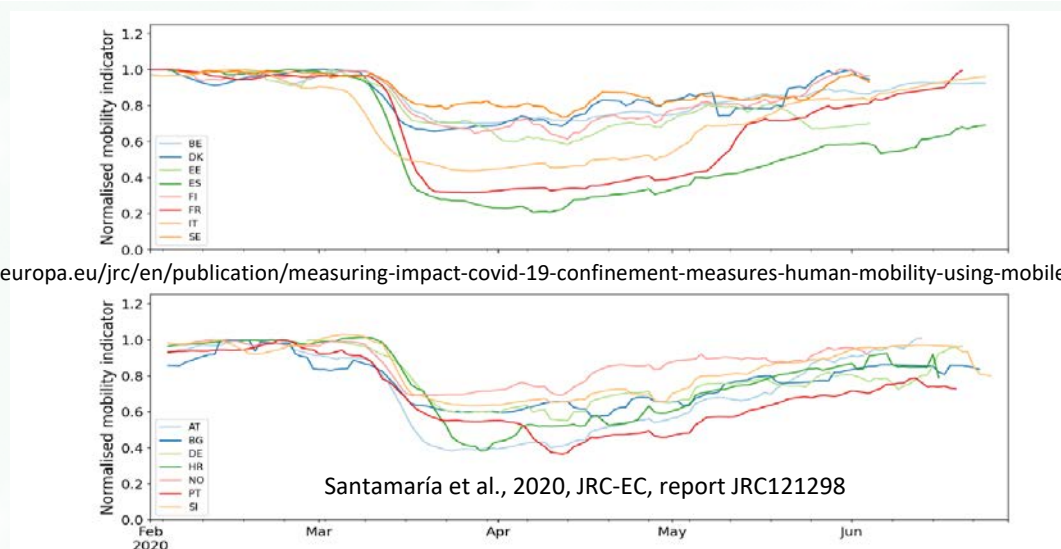
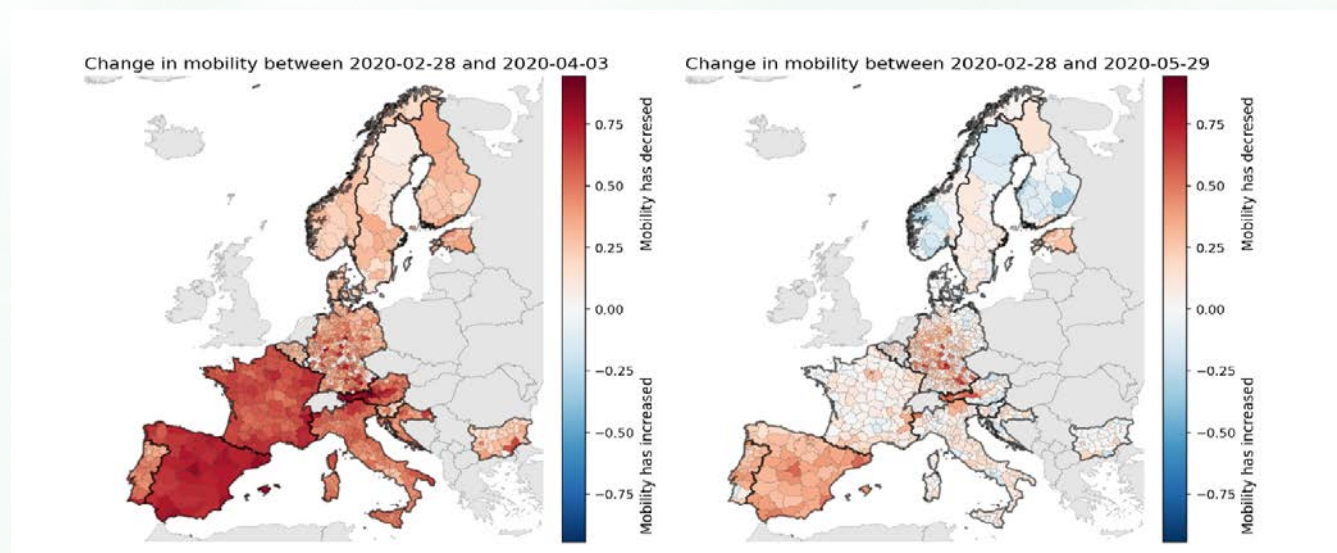
Alkenes	heptene 100 µg O ₃ m ⁻³ octene 41 µg O ₃ m ⁻³	Aromatic Hy.	toluene 21 µg O ₃ m ⁻³ m,p- & o-xylene 9 & 8 µg O ₃ m ⁻³ 1,3,5 trimethylbenzene 5 µg O ₃ m ⁻³
Aromatic Hy.	Toluene 40 µg O ₃ m ⁻³ , 1,3,5,-trimethylbenzene 21 µg O ₃ m ⁻³ , o- & m,p-xylene 17 & 14 µg O ₃ m ⁻³	Alkenes	heptene 11 µg O ₃ m ⁻³ octene 5 µg O ₃ m ⁻³
Terpenes	camphene & a-pinene 16 & 11 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 a-pinene 6, µg O ₃ m ⁻³ camphene 6 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)		Terpenes	
Aromatic Hy.	o,m,p xylenes & toluene 17 µg O ₃ m ⁻³ together, ethylbenzene, trimethylbenzene 4 µg O ₃ m ⁻³ together		
Terpenes	camphene & m-cymene 6 µg O ₃ m ⁻³ β-pinene µg O ₃ m ⁻³ octene 3 µg O ₃ m ⁻³		
Alkenes	dimethylbutane (3 µg O ₃ m ⁻³)		
Alkanes	formaldehyde & butiraldehyde 4 µg O ₃ m ⁻³ together		
Aldehydes	sabinketona 2 µg O ₃ m ⁻³		
Ketones			

JULY 2022: PUERTOLLANO, EUSKADI, VALENCIA

O₃ & COVID19 PANDEMIC

Changes in total mobility caused by COVID19 lockdown in Europe



<https://ec.europa.eu/jrc/en/publication/measuring-impact-covid-19-confinement-measures-human-mobility-using-mobile-positioning-data>

Santamar a et al., 2020, JRC-EC, report JRC121298

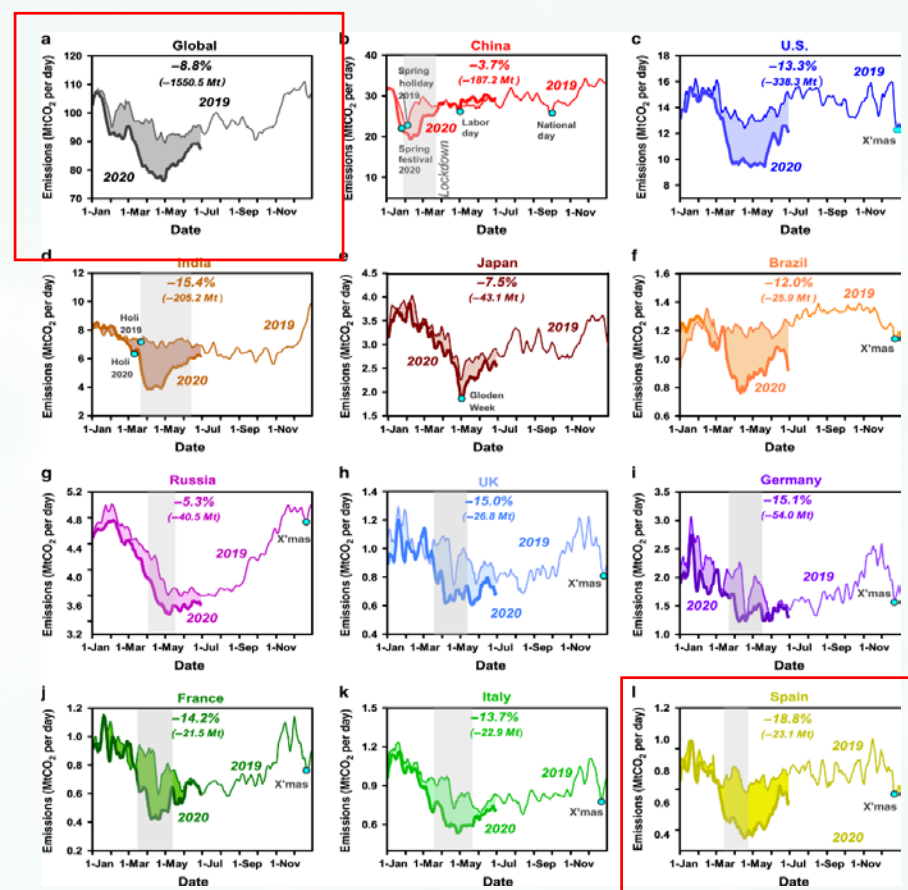
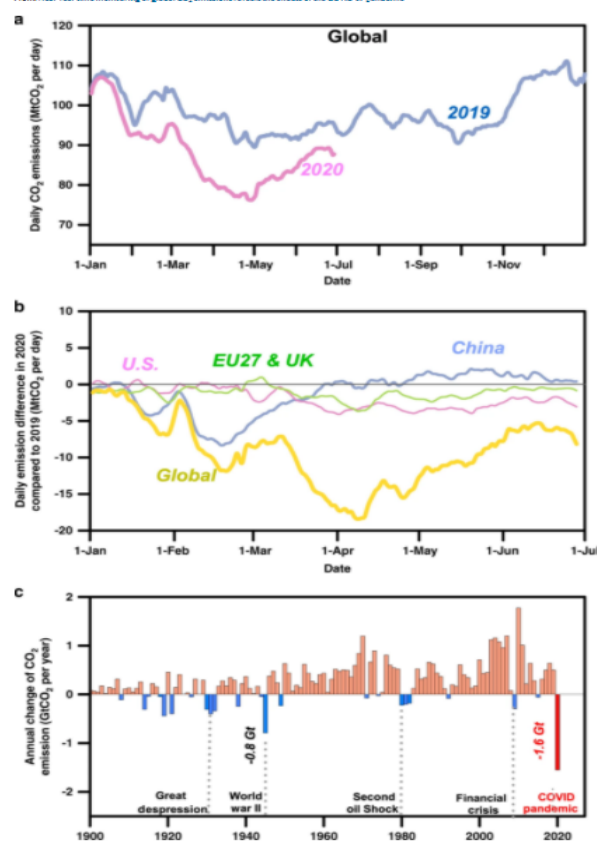
O₃ & COVID19 PANDEMIC

Change in worldwide fossil fuel combustion CO₂ emissions

Liu, Z., Ciais, P., Deng, Z. *et al.* Near-real-time monitoring of global CO₂ emissions reveals the effects of the COVID-19 pandemic. *Nat Commun* **11**, 5172 (2020). Published 14 October 2020

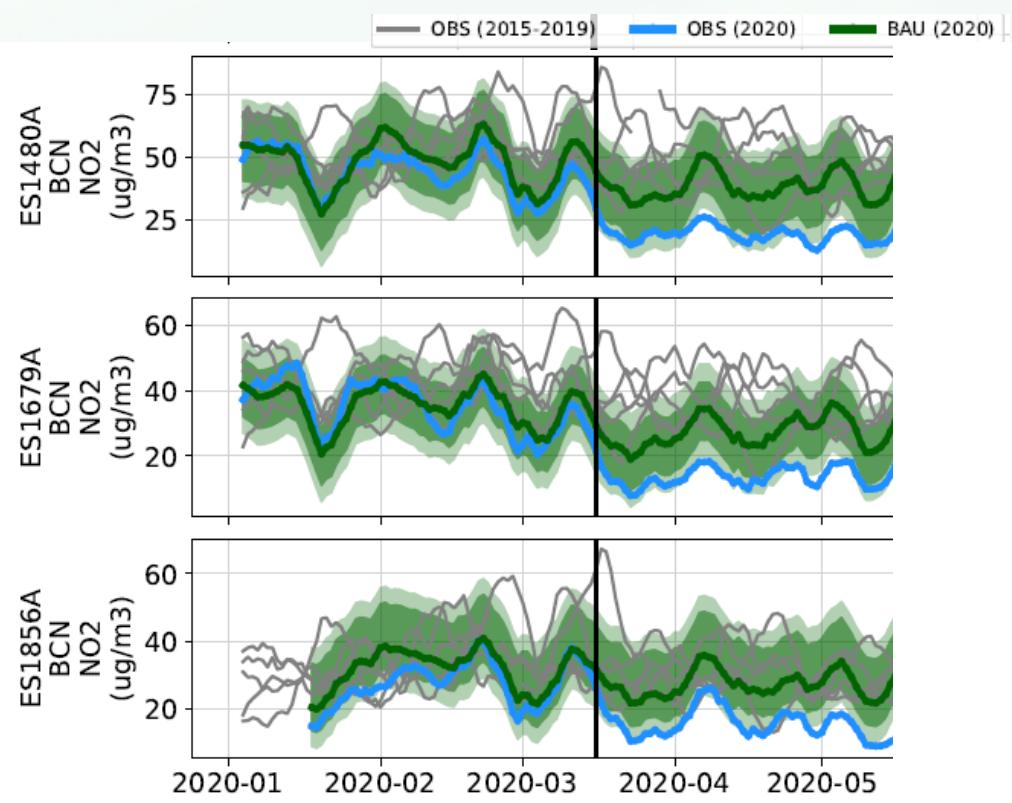
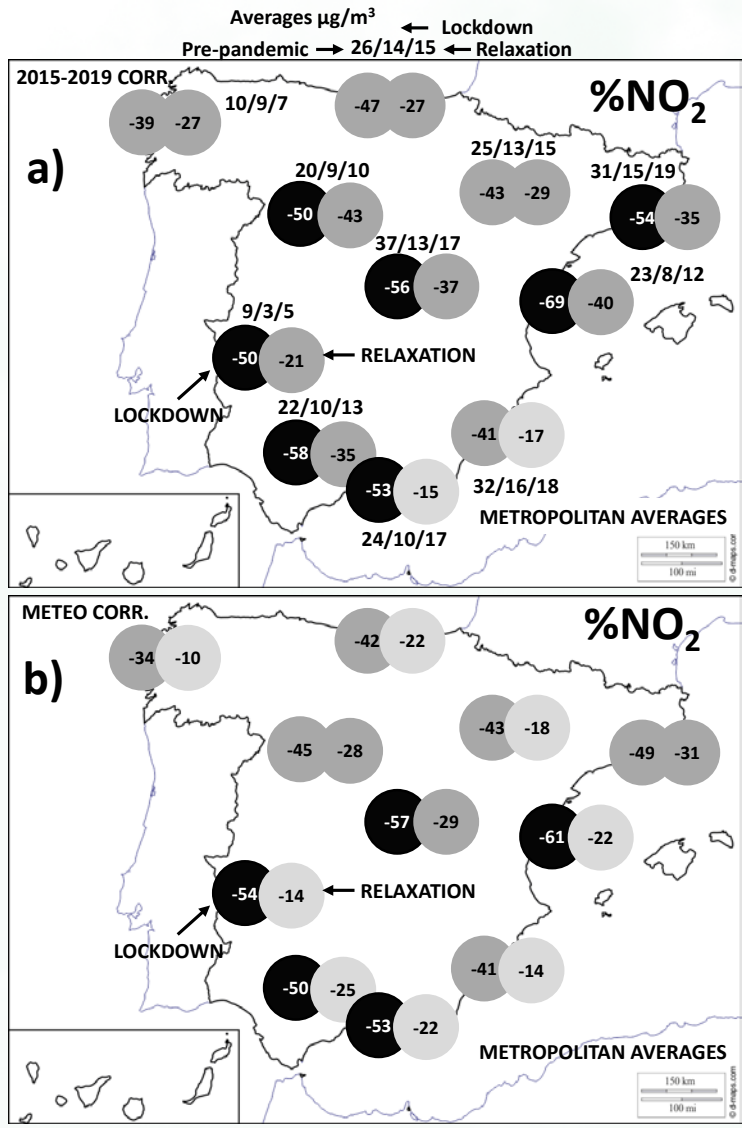
Fig. 1: Effects of COVID-19 on global CO₂ emissions.

From: 'Near-real-time monitoring of global CO₂ emissions reveals the effects of the COVID-19 pandemic'



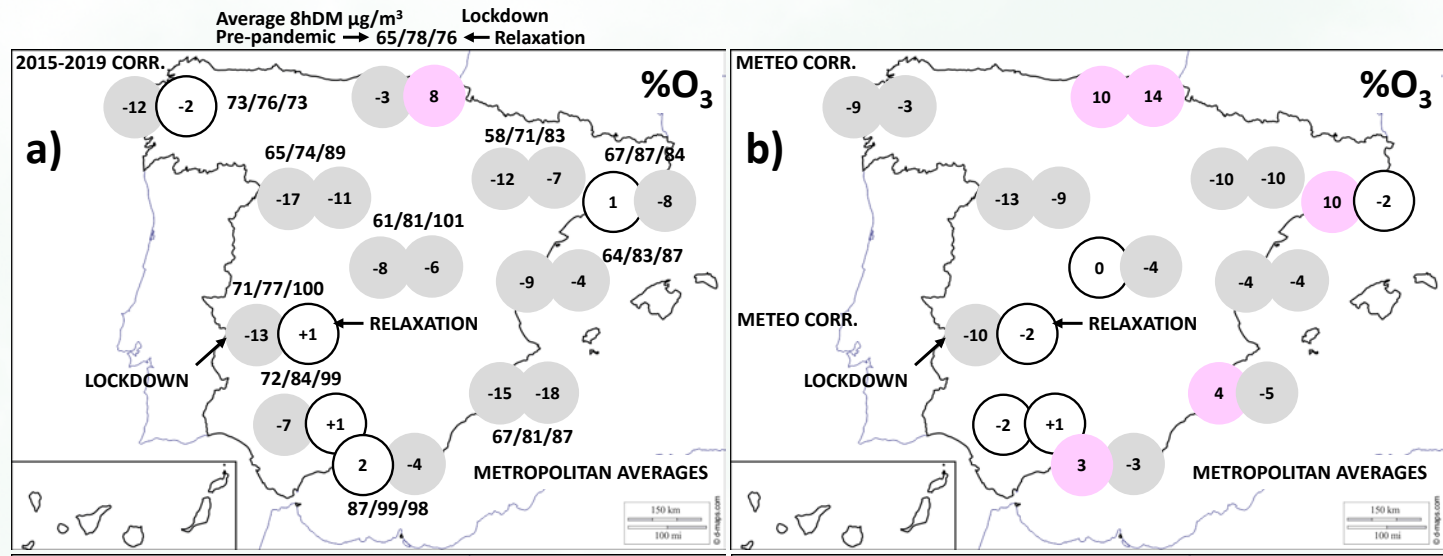
The key result is an abrupt 8.8% decrease in global CO₂ emissions (-1551 Mt CO₂) in the first half of 2020 compared to the same period in 2019.

O₃ & COVID19 PANDEMIC



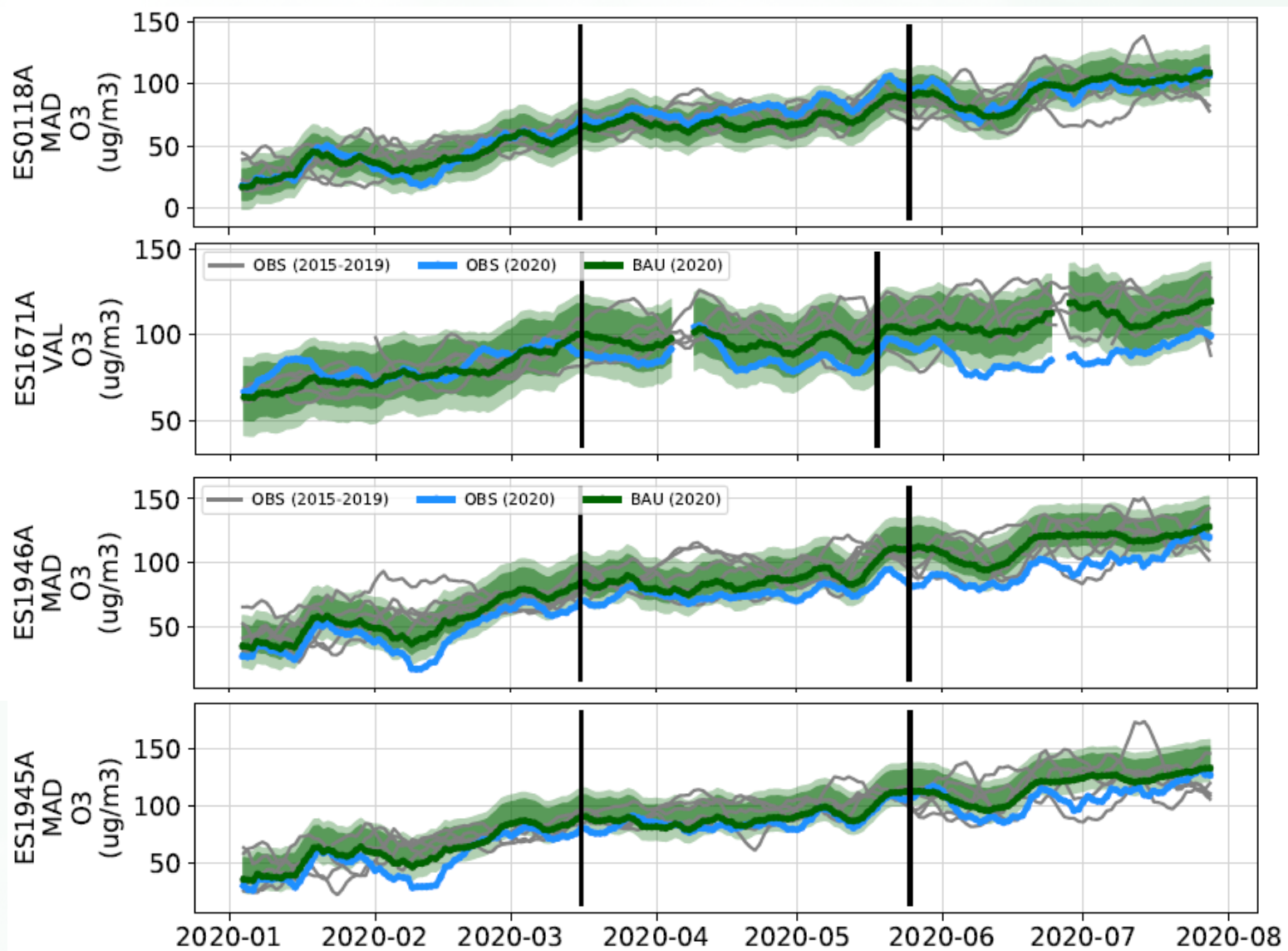
Querol X., et al., 2021. Sci Total Environ.

O₃ & COVID19 PANDEMIC



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

O₃ & COVID19 PANDEMIC



Traffic site Madrid E. Aguirre

Rural receptor Valencia Villar Arz.

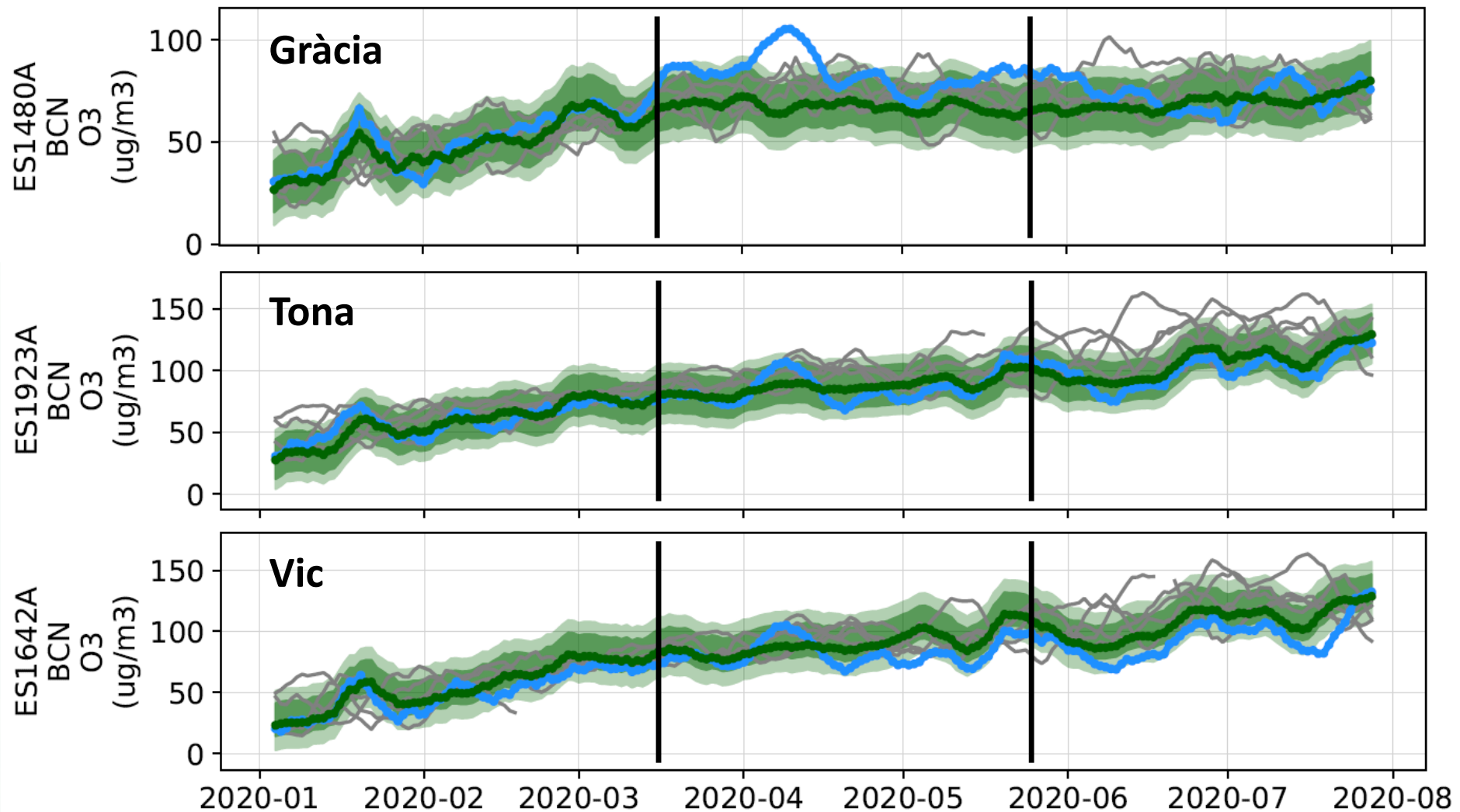
Sub urban receptor Madrid-J.Carlos I

Sub urban receptor Madrid-El Pardo

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

O₃ & COVID19 PANDEMIC

PRECURSORS ABATEMENT MEASURES IMPLEMENTED FROM MAY TO JULY MAY BE EFFECTIVE IN R3 ZONES



MAJOR LESSONS LEARNT

1. Complex O_3 phenomenology known since 1990s (**Millán et al. 1997 and successive studies**)
2. Basins of Madrid, N-Barcelona, N-Tarragona, València-Castelló, Puertollano, Guadalquivir tend to record the highest O_3 for specific parameters and environments
3. Specific VOCs with high O_3 formation potential are identified in each basin. Emission abatement should focus on these
4. COVID19 lockdown reduced O_3 during June-July (high O_3 season) in 4% as an average for cities and 10% as an average for the receptor areas, with road traffic being reduced by 20-25%: May-July measures can have an effect
5. We need to use critical loads criteria: Many sources of precursors in a given region, all them meeting emission standard requirements, might still cause a problem due to the high emissions density and more stringent emission limit values should be implemented in the O_3 season
6. These measures are very relevant in R3 zones, but also in R1 and R2 contributing to the O_3 background
7. Spring-Summer biomass burning (agricultural and forest fires) can also contribute importantly to rise O_3

MOLTES GRÀCIES !



xavier.querol@idaea.csic.es



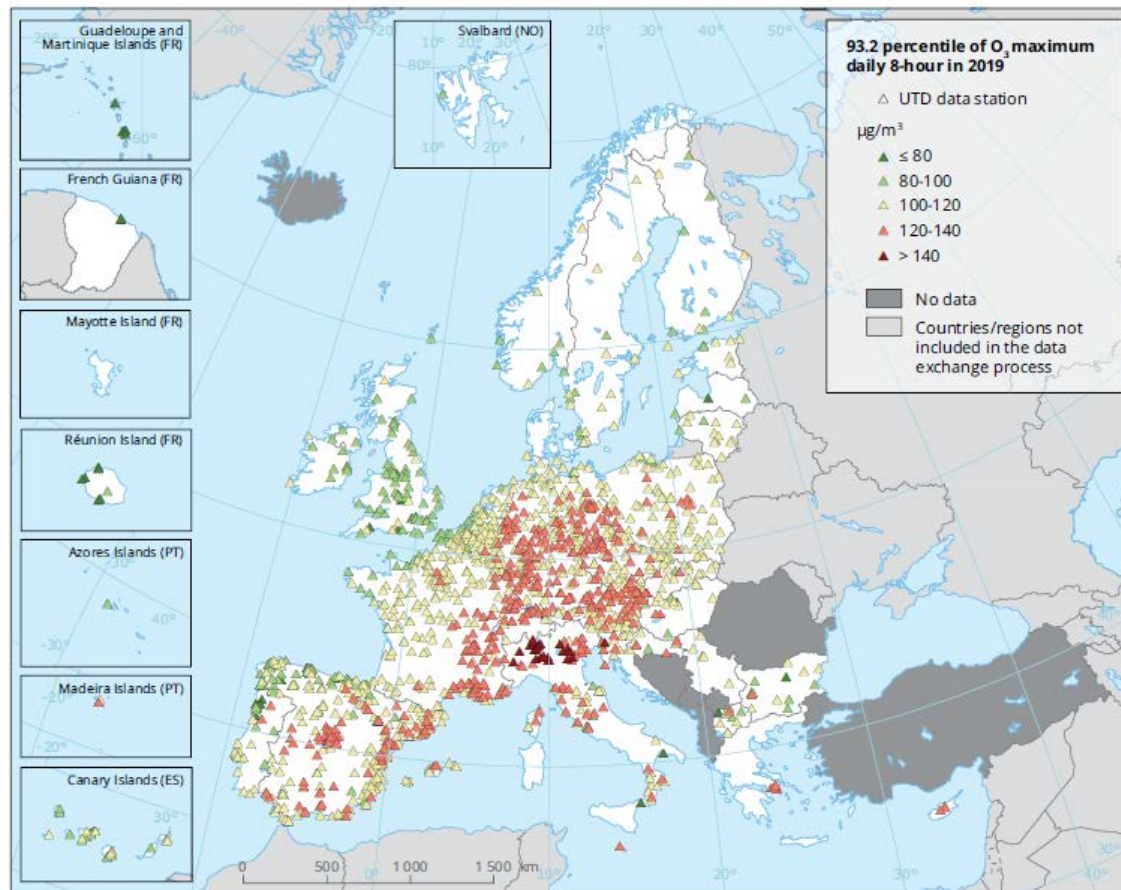
LEVELS OF O₃ IN SPAIN

O₃ triennial target value 2019

EEA Report | No 09/2020

23/11/2020

European Environment Agency



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MINISTERIO
PARA LA TRANSICIÓN ECOLÓGICA
Y EL RETO DEMOGRÁFICO

Ozono. Protección de la Salud

VO Salud 120µg/m³ < 25 ocasiones

<VOLP
>VOLP <=VO
>VO

