Supplement of:

Drivers of divergent trends in tropospheric ozone hotspots in Spain, 2008–2019

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S1. General supplemental data

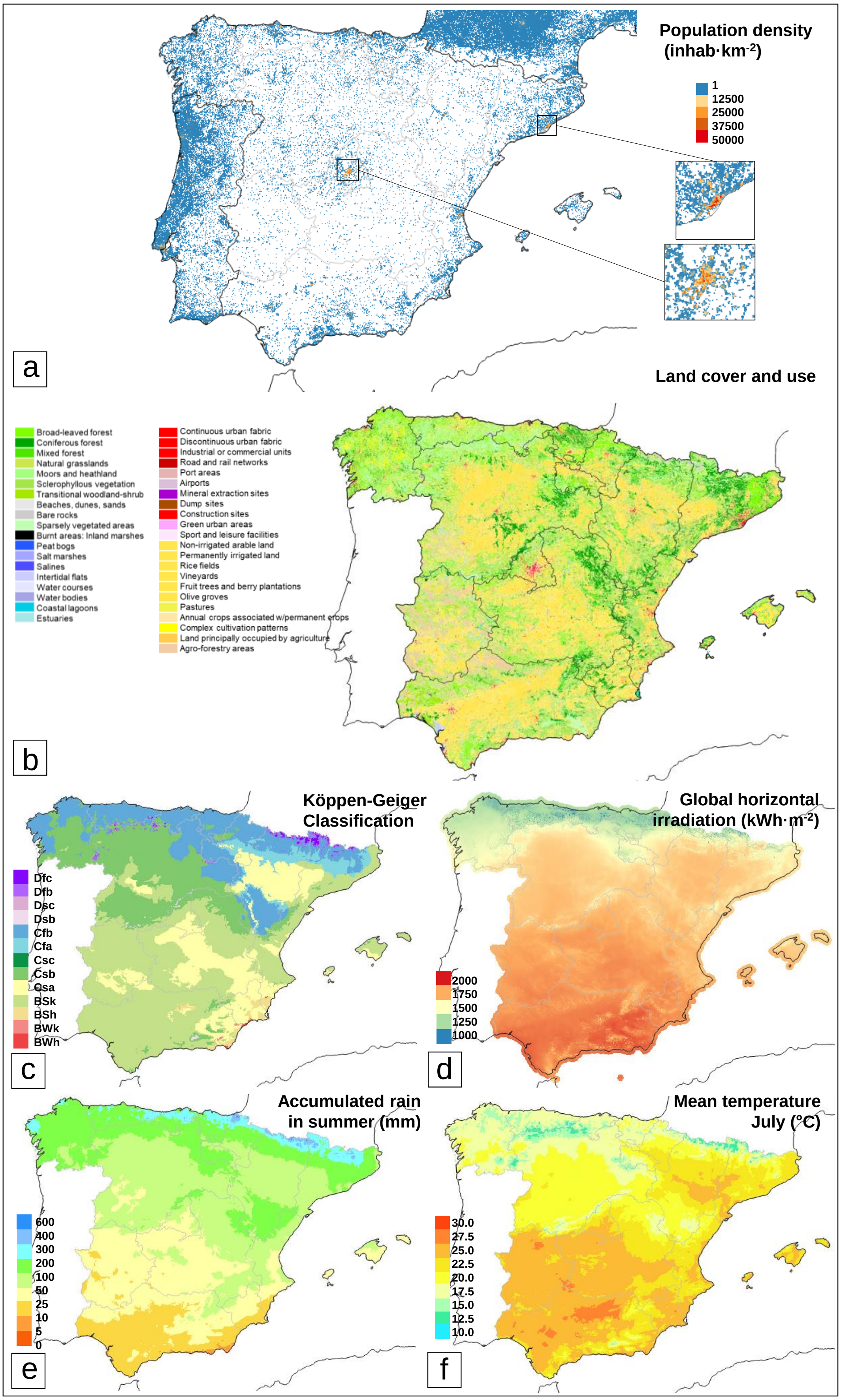


Figure S1.1. (a) Population density (modified after Batista et al., 2021)—some districts in Barcelona and Madrid are the most densely populated in Europe. (b) Land cover and land use (EUROSTAT, 2018)—half of Spain's territory is woodland, 27% cropland, 13% grassland, 6% water bodies, and 4% artificial. (c) Köppen–Geiger climate classification––in this classification, southern Spain is predominantly temperate, with hot, dry summers (CSa), with a Mediterranean littoral climate in Cataluña and the Valencian Community, cold steppe (BSk) in the area influenced by the Ebro River (north-eastern Spain), temperate with mild, dry summers (CSb) in Castilla y León, and temperate with no dry season and mild summers (Cfb) in the northern areas (AEMET, 2018). (d) Global horizontal irradiation (modified after Solargis, 2019). (e) Average accumulated rain in summer. (f) Average temperatures in July. (c, e, and f modified after AEMET, 2018).

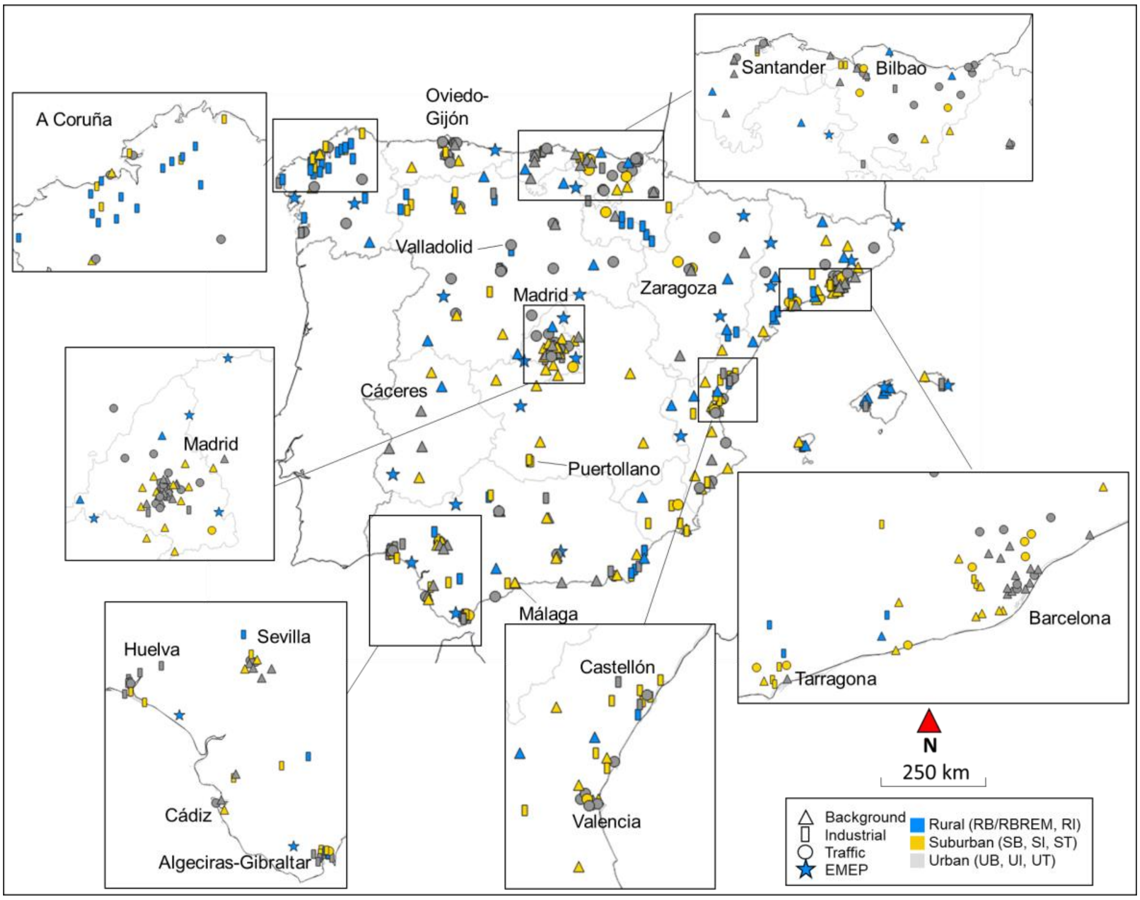


Figure S1.2. Area of study and locations of the 414 monitoring stations (AQMSs) classified by type of surrounding area (different colors for rural, suburban, and urban) and type of predominant nearby emissions sources (different shapes for traffic, industrial, and background). UT/UI/UB—urban (traffic/industrial/background), ST/SI/SB—suburban (traffic/industrial/background), and RB/RI/RBREM—rural (background/industrial/regional background). See Table S1.1 for detailed information. Among the 414 AQMSs used for the present-day assessment, up to 319 were used to assess the trends, depending on data availability.

Table S1.1. Number of AQMSs per type. UT/UI/UB—urban (traffic/industrial/background), ST/SI/SB—suburban (traffic/industrial/background), and RB/RI/RBREM—rural (background/industrial/regional background).

Trend assessment (2008–2019)

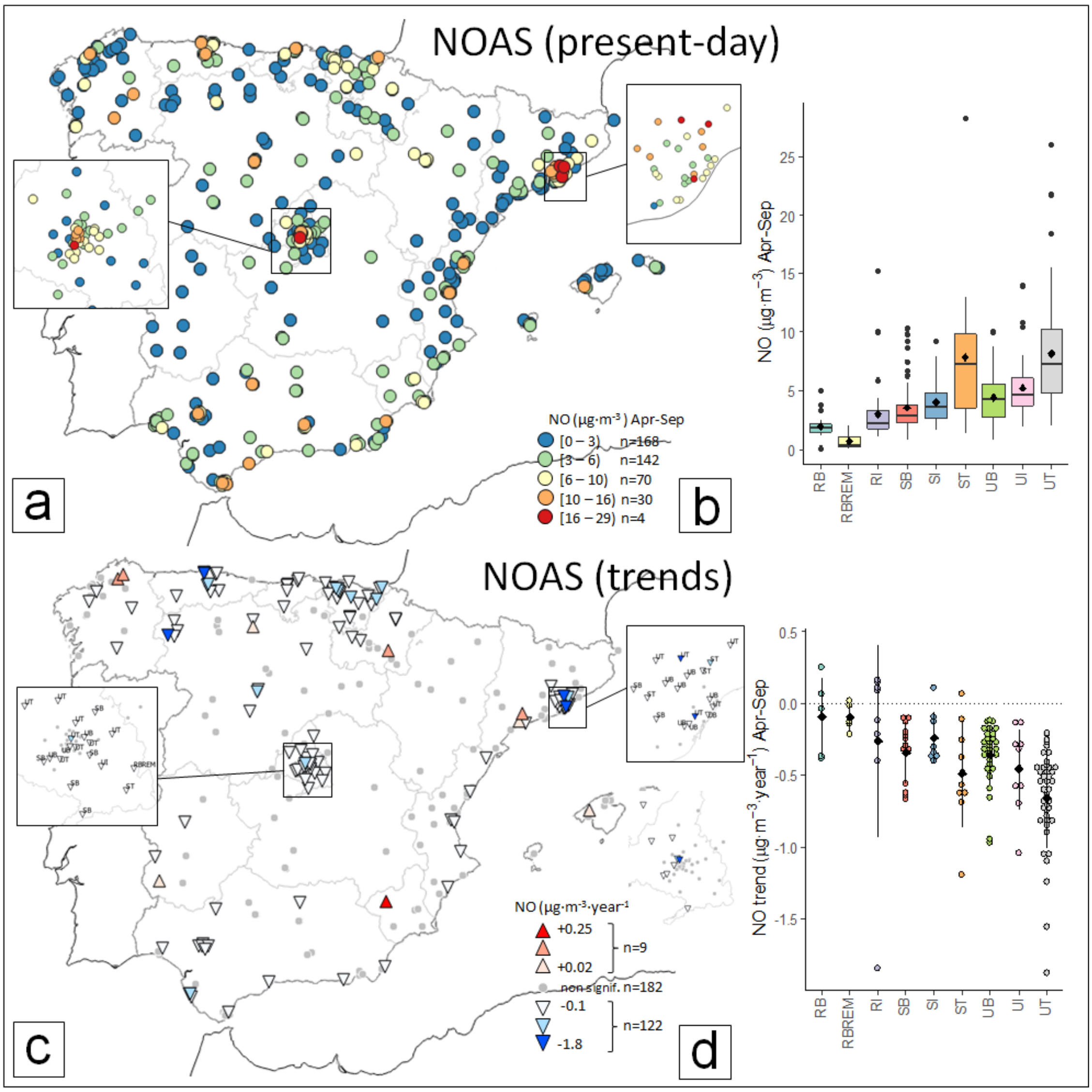
	Rural			Suburban			Urban			TOTAL
Metric	**RB**	**RBREM**	**RI**	**SB**	**SI**	**ST**	**UB**	**UI**	**UT**	
NOAS	20	20	27	44	35	16	54	25	72	313
NO2AS	20	20	27	45	36	16	55	27	73	319

Present-day assessment (2015-2019)

	Rural			Suburban			Urban			TOTAL
Metric	**RB**	**RBREM**	**RI**	**SB**	**SI**	**ST**	**UB**	**UI**	**UT**	
NOAS	32	24	42	61	51	17	65	36	86	414
NO2AS	32	24	42	61	51	17	65	36	86	414

Table S1.2 Number of stations used and trends detected

Metric	Present-day (2015–2019) (number of AQMS with valid data used)	Trends (2008–2019) (number of AQMS used)	% of AQMS with trends	Number of AQMS with up and down trends		% of AQMS with up and down trends		% of trends (within the AQMS with trends)	
				↑	↓	↑	↓	↑	↓
NOAS	414	313	39%	9	122	3%	39%	7%	93%
NO2AS	414	319	40%	1	129	~0%	40%	1%	99%



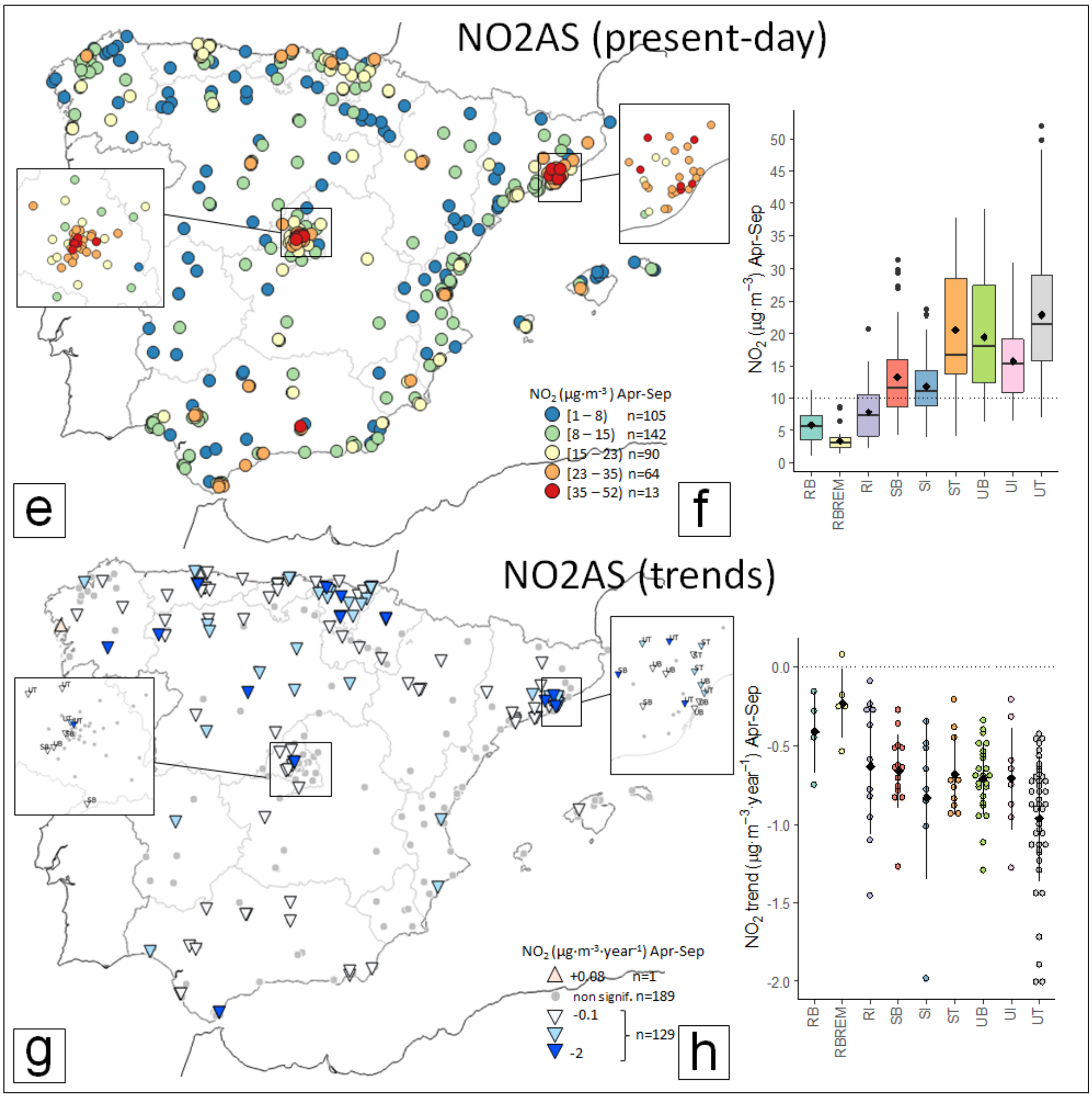


Figure S1.3. (a and b) Present-day (2015–2019) NO concentrations (µg·m⁻³) for April–September from the 414 stations with valid data; (a) spatial variation; (b) box-plot by station type; (c and d) statistically significant (p<0.05) trends in NO concentrations (µg·m⁻³·year⁻¹) for April–September (2008–2019) from the 313 stations with valid data; (c) spatial variation in the trends; (d) annual variation by station type. Circles—trends from individual stations, black squares—averages, black lines—standard deviations; (e–h) Same captions as for (a–d), but for NO_2 instead of NO. For the NO_2 trends (g and h), data from the 319 stations with valid data were included. Horizontal lines in (f)—annual 10 µg·m⁻³ Guideline Values (WHO, 2021).

Table S1.3. Ground-level NO and NO_2 variations. Only the trends with statistical significance ($p<0.05$) are shown for all types of stations and for only traffic stations (suburban and urban). In parentheses, "n=x" is the number of stations used and "sd=x" is the standard deviation of the variations

		relative slope (%·year^{-1})	absolute slope (µg·m^{-3}·year^{-1})
NO	**all stations**		
	Madrid (n=21)	-5% (sd=1)	-0.4 (sd=0.2)
	Barcelona (n=18)	-3.5% (sd=1)	-0.5 (sd=0.4)
	only traffic		
	Madrid (n=10)	-4.8% (sd=0.8)	-0.47 (sd=0.2)
	Barcelona (n=9)	-3.6% (sd=1.1)	-0.7 (sd=0.5)
NO_2	**all stations**		
	Madrid (n=8)	-3% (sd=0.7)	-0.8 (sd=0.4)
	Barcelona (n=22)	-2.4% (sd=1.8)	-0.8 (sd=0.5)
	only traffic		
	Madrid (n=4)	-3% (sd=0.6)	-1 (sd=0.4)
	Barcelona (n=9)	-2.5% (sd=0.6)	-1 (sd=0.5)

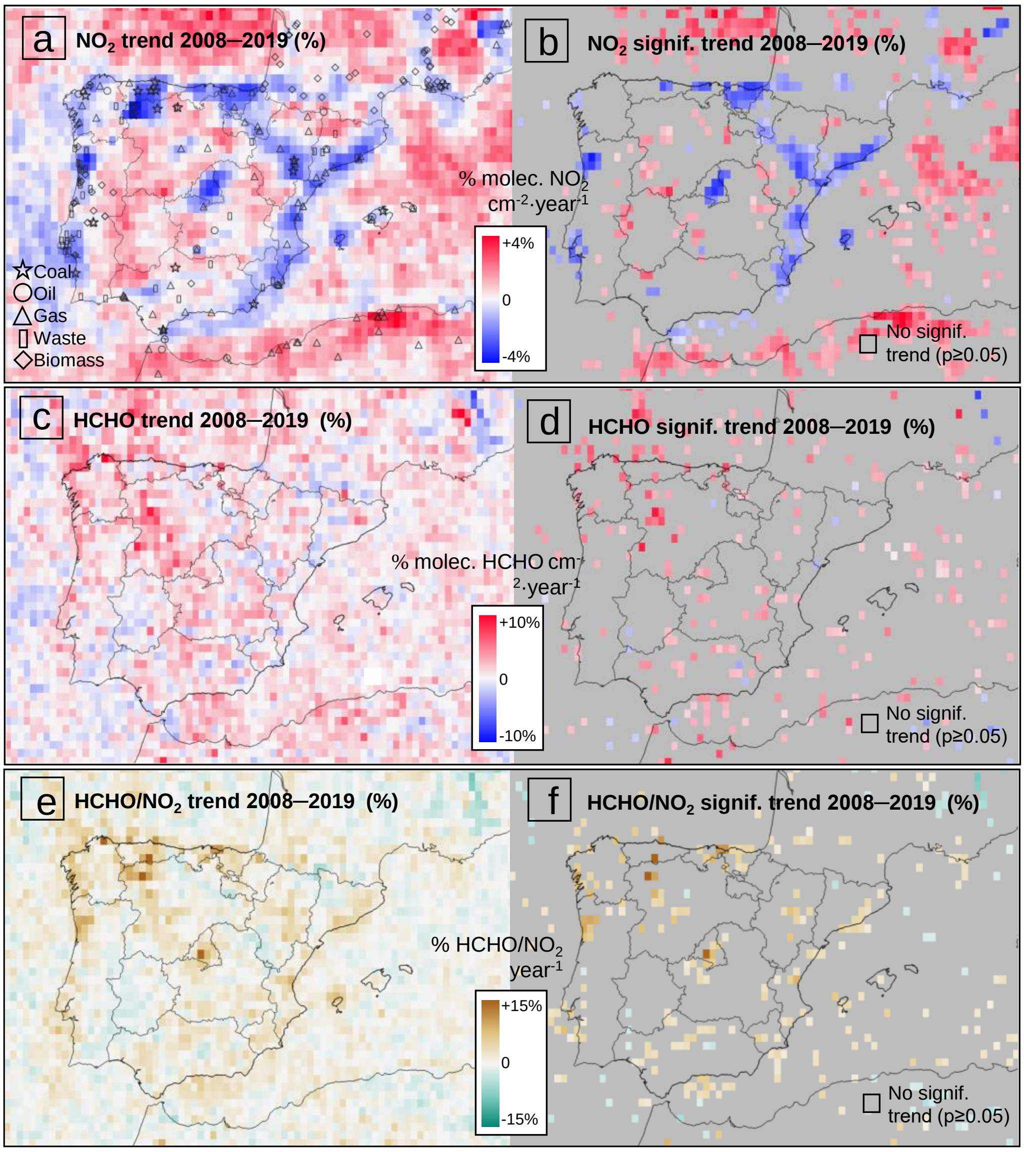


Figure S1.4. Spatial distribution of NO_2, HCHO and HCHO/NO_2 tropospheric columns for April–September measured by OMI–NASA, and HCHO/NO_2 ratio. Each pixel covers an area of 13×24 km^2. (a, c, and e) relative trends (%) for 2008–2019; and (b, d, and f) relative trends (%) for 2008–2019 showing only pixels with statistically significant ($p<0.05$) trends (gray pixels—$p\geq0.05$). Absolute variations can be found in Figure 3 in the main text. The map in (a) shows the locations of power plants operational in 2018 (from Byers et al., 2021).

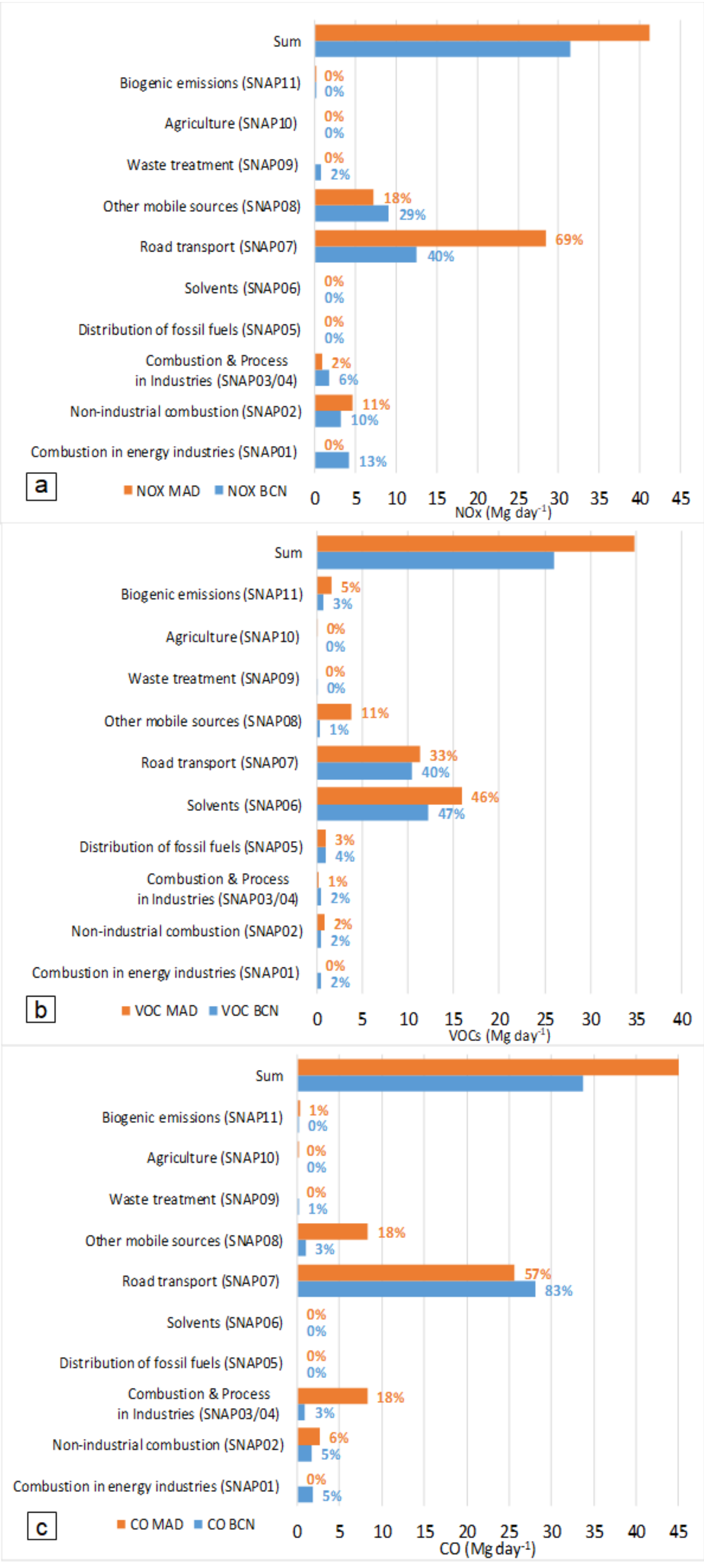


Figure S1.5. (a) NOx; (b) VOCs (non-methane); and (c) CO emissions from Madrid (MAD) and Barcelona (BCN) in 2011 (data from Soret et al., 2014). Bar length—absolute value (according to the x-axis), and percentage—proportion of each sector to the total emissions (column 'Sum'). Note the sector names are different from those used in the text as, here, they are expressed in the SNAP convention, with the EEA data used for the calculations using the EEA aggregated sector names. See: https://www.ceip.at/fileadmin/inhalte/ceip/00_pdf_other/2019/06122019_conversiontablereportingcodes_.xlsx and Appendix 4 in https://www.eea.europa.eu/publications/european-union-emissions-inventory-report for useful conversion tables. According to these, the solvents sector (SNAP06) is included in the industry sector considered in the main manuscript, which uses the EEA classification sector.

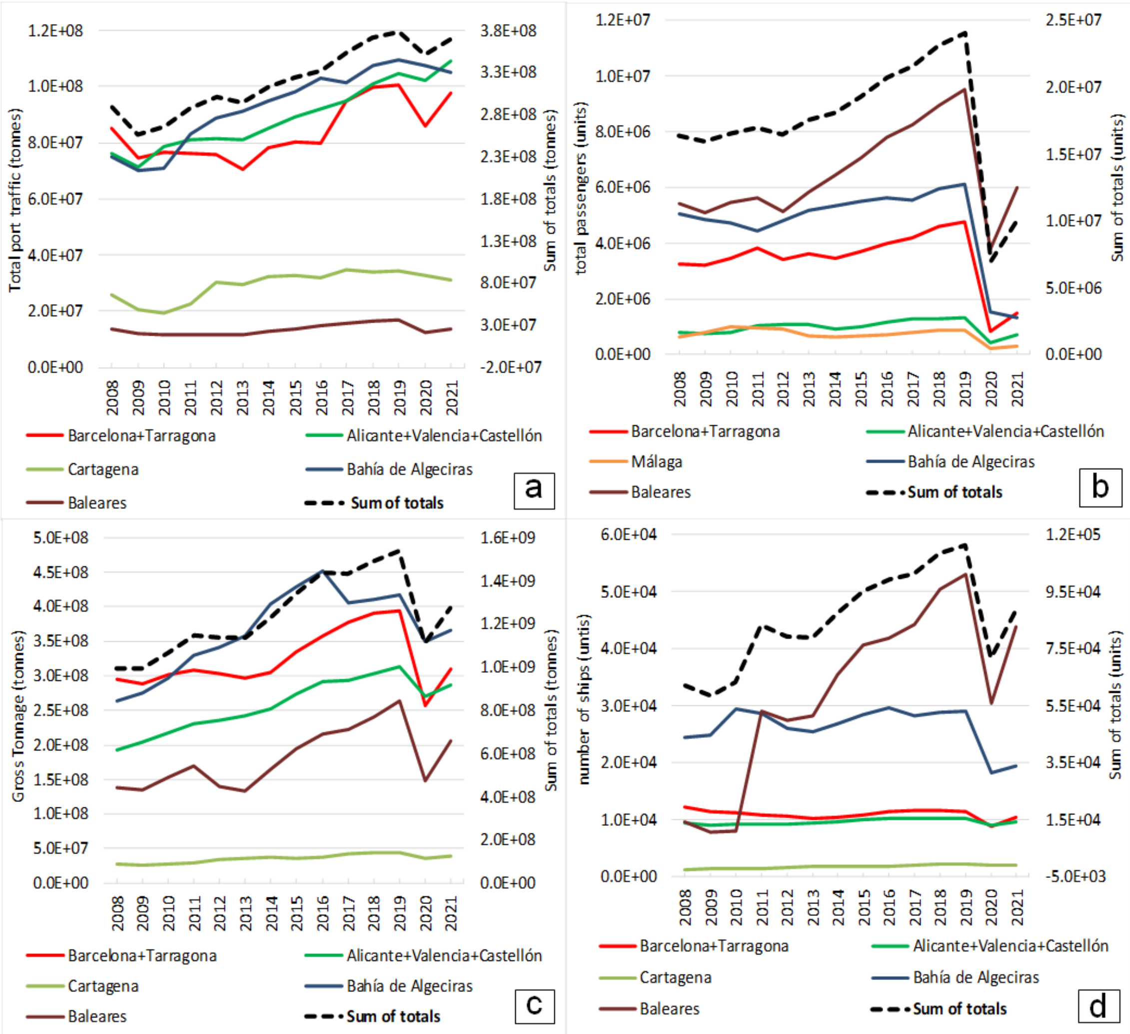


Figure S1.6. Shipping data for the main ports along the Spanish Mediterranean coast and Alborán Sea for 2008–2021 (data from Puertos del Estado, 2022). Only the top five ports per metric are shown. (a) Total port traffic; (b) total passenger numbers; (c) gross tonnage; and (d) number of ships.
(https://www.puertos.es/es-es/estadisticas/Paginas/CuadroMando_anual.aspx)

S2. Data processing and screening

S2.1 Data from monitoring stations (NO and NO_2)

For the air quality monitoring stations (AQMSs), we defined the years with valid data to be those having at least 75% of the hourly records available, following similar criteria used in previous studies (e.g., Fleming et al., 2018; Lefohn et al., 2018). We applied this data-capture threshold to all averaging levels. See Table S1.1 for the number of AQMSs used, categorized by their respective types in each analysis.

We used the AQMS classification outlined in Decision 2011/850/EU, considering the environment represented by each station (and the predominant nearby emissions sources)—urban (traffic, industrial or background), suburban (traffic, industrial or background), and rural (industrial, background or regional background). Within the rural regional background sites, it is worth noting that 13 sites are part of the European Monitoring and Evaluation Program (EMEP) network.

The air-quality data used here is available at:
https://www.miteco.gob.es/en/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/calidad-del-aire/evaluacion-datos/datos/Datos_2001_2020.aspx, where hourly records of ground-level pollutant concentrations are compressed in CSV files per year and pollutant, together with biannual meta-files with information on the AQMSs. Using an R program developed specifically for this study, we downloaded, extracted, decoded, and organized the data into formats prepared for subsequent calculations.

Although all the air-quality data used in this study passed quality checks before being reported to the European Community (MITERD, 2019), we analyzed key statistical values per station and year to screen for possible incorrect values. We also carefully analyzed the outliers and removed them if physically impossible.

S2.2 Satellite-based data (OMI–NASA)

For the spaceborne QA4ECV NO_2 and HCHO data measured by OMI–NASA, see http://www.temis.nl/qa4ecv/no2.html and https://www.temis.nl/qa4ecv/hcho.html, which has information on data screening and the checks performed. The data are already corrected and directly usable.

S2.3 Emissions data of O_3 precursors from inventories

The data on emissions from the EU-28 (before Brexit) and Spain can be accessed directly from the following links:

Data on NOx, VOCs (non-methane) and CO available at: https://www.eea.europa.eu/data-and-maps/dashboards/air-pollutant-emissions-data-viewer-4

Data on CH_4 available at: https://www.eea.europa.eu/data-and-maps/data/national-emissions-reported-to-the-unfccc-and-to-the-eu-greenhouse-gas-monitoring-mechanism-18

S2.4 Data on meteorological parameters (ERA5)

The ECMWF meteorological data (ERA5 reanalysis) can be found at:
https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-levels-monthly-means?tab=overview

The meteorological parameters we used were, 2-m temperature (ERA5 code: t2m), surface solar radiation downward (ssrd), downward UV radiation at the surface (uvb), boundary layer height (blh), total cloud cover (tcc), 10-m wind speed (si10), evaporation (e), surface pressure (sp), and total precipitation (tp). Some parameters we used (solar radiation, evaporation, and precipitation) were accumulated over a particular time period (https://confluence.ecmwf.int/display/CKB/ERA5%3A+data+documentation). For the monthly averaged reanalysis data we used, the accumulation period was 1 day. Thus, we multiplied each "1 day" value by the number of days in each month to obtain the accumulated monthly value, and then summed it for every April to September period to obtain annual (seasonal) values. For the rest of the parameters, these seasonal values were obtained by averaging the monthly data from April to September. The remaining calculations were made as described in the section "Methodology" in the main manuscript to obtain present-day data and to estimate the trends.

S3. Assessment of meteorological parameters

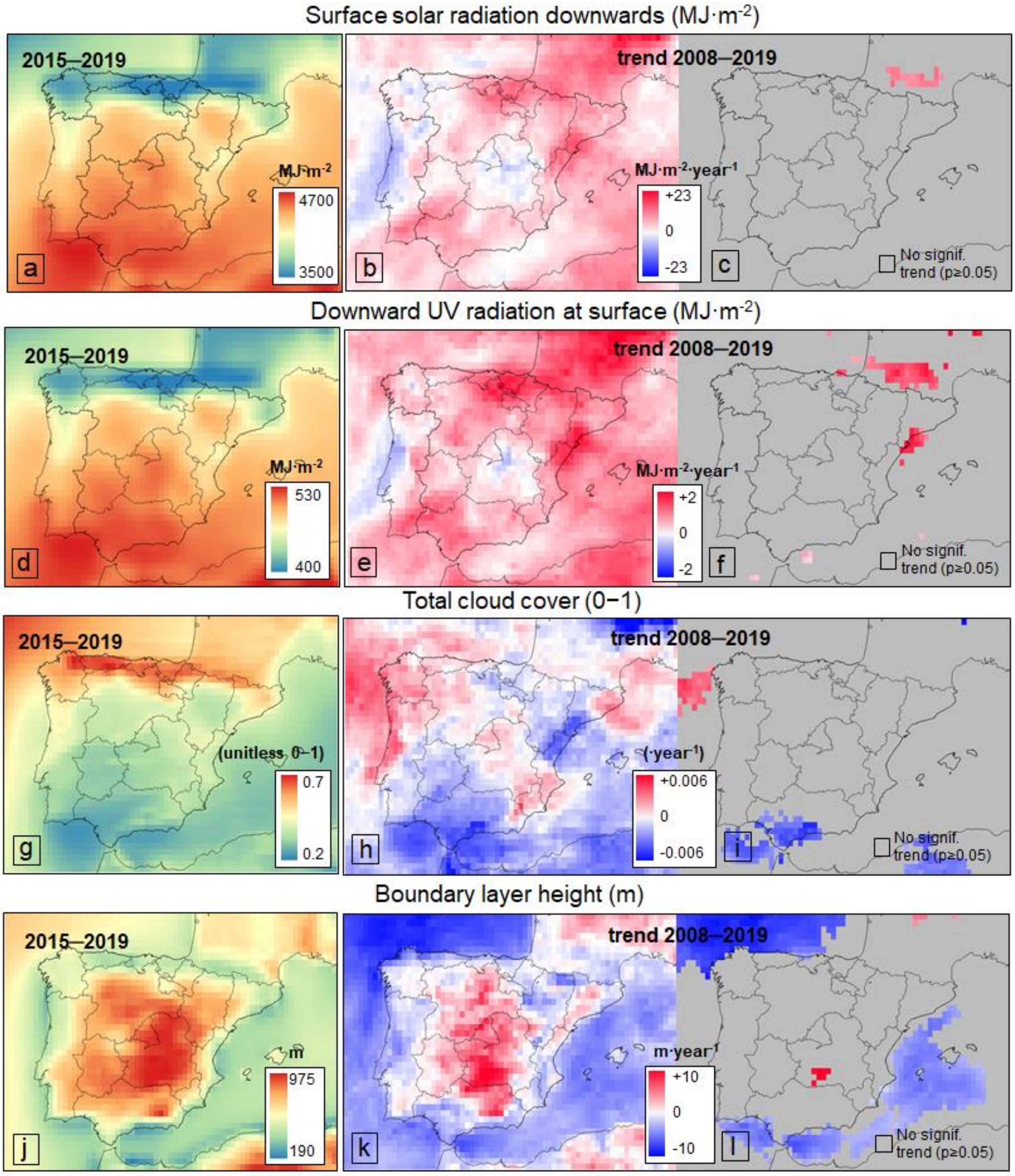


Figure S3.1. Meteorological parameters relevant to O_3 (aggregations for April–September). The leftmost column shows the present-day (2015–2019) spatial distributions, the middle column illustrates the changes that occurred during 2008–2019, and the rightmost column indicates which of these changes were statistically significant ($p<0.05$). (Calculated from ERA5 monthly averaged data). Cont'd. below.

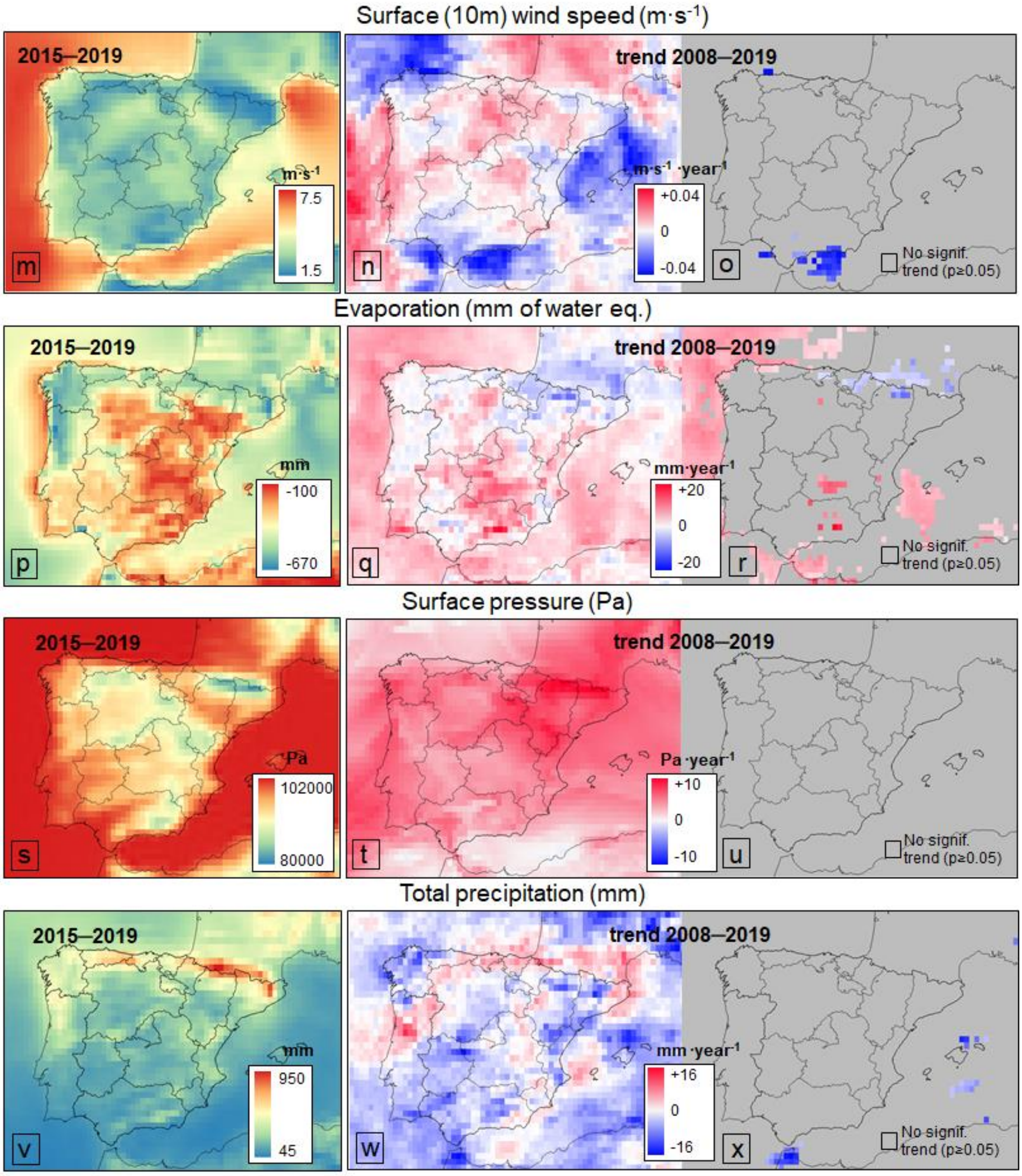


Figure S3.1. Cont'd..

S4. Summary of NOx emission policies and regulations

Across Europe, a comprehensive framework of initiatives, policies, and regulations addresses NOx and other O_3 precursor pollutant emissions. The European Union Emissions Trading System (EU ETS) sets emissions caps for industries [https://climate.ec.europa.eu/eu-action/eu-emissions-trading-system-eu-ets_en], reinforced by the Industrial Emissions Directive (2010/75/EU), which promotes Best Available Techniques (BAT) [https://joint-research-centre.ec.europa.eu/scientific-activities-z/sustainable-production-best-available-techniques_en]. Sector-specific guidance in the form of Technical Reference Documents (BREFs) is instrumental in tackling NOx pollution and improving air quality. National emission limits are established through the National Emission Ceilings Directive (2001/81/EC and 2016/2284/EC). The Clean Air Policy Package targets emissions from various sources, with a specific emphasis on increasingly stringent EURO vehicle emission standards (e.g., 2007/715/EC).

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