Atmospheric Environment 79 (2013) 705–715

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities

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HIGHLIGHTS

- We calculate annual trends for ozone and associated statistics.
- We discuss of spatial distribution of levels and changes in ozone concentrations.
- We use an innovative method by co-kriging to map results.
- We discuss of possible explanations of observed trends.
- We discuss of the convergence of ozone pollution at remote and urban sites all around the Mediterranean Europe.

ARTICLE INFO

Article history:
Received 16 May 2013
Received in revised form
16 July 2013
Accepted 17 July 2013

Keywords:
Mann–Kendall test
Ground-level ozone
Mediterranean basin
Trend
O_3

ABSTRACT

Analyzing hourly ozone data from 214 European background sites over the time period 2000–2010, we demonstrated for the first time that the ozone control measures are effective at rural sites, while ozone concentrations are still increasing in the cities. The Western European Mediterranean basin is expected to be more strongly affected by climate change, including ozone pollution, than most of the other regions of the world. At 58% of the rural sites significant decreases were found resulting in an average − 0.43% per year while an increase was recorded in urban and suburban stations (+0.64% year^{-1} and +0.46% year^{-1}, respectively). At cities ozone average levels increased, but the peak ozone concentrations decreased. In all station types, a significant reduction in the amplitude of peak ozone concentrations was found at more than 75% of stations (98th percentile, −0.77% year^{-1}; hourly peak, −1.14% year^{-1} and daily average peak, −0.76% year^{-1}). The peak reduction may largely be attributed to the reduction in NO_x and VOC emissions within the European Union which started in the early 1990s. The results suggested a convergence of ozone pollution at remote and urban sites all around the Western European Mediterranean basin.

1. Introduction

Ground-level ozone (O_3) is an important atmospheric pollutant and climate forcer. The majority of surface ozone formation occurs when nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) react in the atmosphere in the presence of sunlight. Ozone, the third important greenhouse gas in terms of radiative forcing (Ramaswamy et al., 2001), is an important air quality issue. The lifetime of tropospheric O_3 varies from one or a few days in the boundary layer to a few tens of days or even a few months in the free troposphere which enables transport from regional to hemispheric scale and hence proportionally greater influence on climate than O_3 near the surface. The localized sources of O_3 precursors and generally short lifetime of surface O_3 make its distribution spatially non-uniform and time-variant (Schwartz, 1989; Zanis et al., 2007). The negative effects of the surface O_3 on human health, crops, forests and materials have been widely discussed since the 1950s (Richards et al., 1958; Mckee, 1994; Krupa et al., 2001; Mills and Harmens, 2011; Dalstein and Vas, 2005,

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http://dx.doi.org/10.1016/j.atmosenv.2013.07.042

2008; Contran and Paoletti, 2007; Paoletti, 2006, 2009; Paoletti and Manning, 2007; Screpanti and De Marco, 2009; De Marco, 2009; Sicard et al., 2011a, 2012).

In view of the harmful effects of photochemical pollution in the lower levels of the atmosphere, the European Council adopted a first Directive on air pollution by ozone in 1992 (92/72/EEC). It established procedures for harmonized monitoring of surface ozone concentrations. An important objective of many environmental monitoring programs is to detect changes or trends in pollution levels over time. More than 20 years later, it is now of interest to verify the effectiveness of the control measures, in lowering both the emission of ozone precursors and the ambient ozone levels.

Following Kourtidis et al. (1997), "natural background" means ozone generated chemically in the troposphere from non-anthropogenic emissions (biogenic and geogenic such as trees, agricultural crops, lightning) plus ozone transported from the stratosphere. Ozone trends are caused by a background hemispheric trend and regional changes (emissions, meteorology…). The establishment of annual ozone trends is important for quantifying the impact of changing precursor emissions and also from the perspective of local and regional air quality control. Rural areas are influenced by the large-scale dispersal of precursors produced at urban and regional scales, and, are the most representative of background pollution at global scale and allow an assessment of the impact on ecosystems (De Leeuw, 2000; Sicard et al., 2009).

The annual cycle and trends of surface ozone at northern and western parts of Europe has been widely studied at rural, suburban and urban sites (Logan et al., 1999; Monks et al., 2003; Vingarzan, 2004; Solberg et al., 2005; Lelieved et al., 2004; Jonson et al., 2006; Derwent et al., 2007; Wilson et al., 2012; Parrish et al., 2012). Since 1950s surface ozone concentrations have increased at background rural sites of the northern mid-latitudes by 1–2% year^{-1} (Logan et al., 1999). In Northern Hemisphere, the ozone levels increased over the Northern Atlantic (Lelieved et al., 2004) producing persistent levels of ozone at rural and urban areas of the European Atlantic Coast (Derwent et al., 2007). Similar trends can be observed at the United States Pacific Coast (Jaffe and Ray, 2007). Significant positive trends in ozone mean concentrations during the 1990s were observed at Northern European rural sites (Vingarzan, 2004). Most sites showed substantial downward trends of high ozone (98 or 95th percentiles) over the past 15 years (Wilson et al., 2012). As an example peak ozone concentrations have decreased by 30% in the United Kingdom (Coyle et al., 2003) and the 99th percentile dropped in Germany between 1990 and 2000 (Beilke and Wilson, 2000).

The Mediterranean basin has many morphologic, geographical and societal characteristics, which make its climate scientifically interesting. Climate change is expected to be more pronounced in the Mediterranean Basin than in most other regions of the world (IPCC, 2001). Whereas temperatures should increase on average by 1.4–5.8 °C worldwide, the difference should be at least 3 °C in the Mediterranean Basin and the Mediterranean Basin will be one of the areas subject to the most drastic reductions in precipitation (IPCC, 2001). Temperatures are expected to continue to increase in the coming decades, with considerable effects on human society and the environment (EEA, 2004). Formation of ozone is dependent on temperature and is higher during the plant growing period (ICP, 2007). A substantial increase in water shortage is expected, due in large part to the increase of temperatures rather than to the decrease in rainfall; therefore, the risk of drought in summer will increase around southern Europe. As O_3 exposure is expected to unbalance water control of vegetation (Paoletti and Grulke, 2010), such climate changes stress once more the importance of a proper assessment of O_3 risk to vegetation, in particular in Mediterranean climate. Overviews of the consequences of climate changes and ozone pollution for trees in the Mediterranean basin are provided by Bakkenes et al. (2002), Petit et al. (2005) and Paoletti (2006).

The European region at highest O_3 risk is the Mediterranean area because of several main reasons. Ozone formation occurs at high temperature in presence of solar radiation, which is elevated in Mediterranean-type ecosystems (Alonso et al., 2001). In summer, anti-cyclonic subsidence, low winds, and strong insolation favor massive photochemical production of O_3, and inhibit recirculation within air masses (Millan et al., 2000). Some areas are subjected to high road traffic and industrial emissions, e.g. the megalopolis/metropolis effect of Marseille in France and Genoa and Milan in Italy (Sicard et al., 2011a).

Surprisingly, however, a comprehensive analysis of surface ozone data and ozone precursor's trends in the Mediterranean Europe has not been carried out. This study aims to characterize and quantify surface ozone concentrations and trends in "67" rural, "74" suburban and "73" urban background sites around the Western European Mediterranean basin (East Spain, Malta, South France and Italy) over the time period 2000–2010, and assess the impact of the changing precursor emission on the time trends.

2. Materials and methods

2.1. Data selection and methodology

Ozone data were kindly provided by the Air quality database AirBase of the European Environment Agency (EEA). Hourly ozone concentrations were obtained for background stations (rural, suburban and urban) over the period 2000–2010 over a strip of land of 200 km along the European coast of the Mediterranean Sea. We selected the stations with more than 75% of validated hourly data per year. The following annual statistics were calculated: 24-h mean concentration, median, 98th percentile, average daily maximum and hourly peak maximum. Over the time period 2000–2010, 214 stations were selected in Spain, France, Italy and Malta. Insufficient station distribution did not allow us to include the Eastern Mediterranean part of Europe into this analysis (data not shown).

Ozone monitoring stations are called urban, when they are located in a city. Residential areas outside a main city represent the suburban zone of a monitoring station. When a station is located outside a city, far from city sources of air pollution, the type of zone is called rural. When the pollution level is not significantly affected by any single source, but by the integrated contribution from all sources upwind of the station, the station is located on a background area (Snel et al., 2004). In order to explore the factors driving the observed surface ozone trends, emission of ozone precursors (namely, $NO + NO_2 = NO_x$, CO and VOC) were examined during both the period 2000–2010 and over a 20-years period (1990–2010). The European emissions are provided by the European Monitoring and Evaluation Programme (EMEP).

2.2. Estimation of annual trends

The Mann–Kendall test is a non-parametric statistical test to detect the presence of a monotonic increasing or decreasing trend within a time series. Data were checked for normal distributions with the Kolmogorov–Smirnov D test. Statistical tests for monotonic trend in ozone time series are commonly confounded by some of the following problems: non-normal data, missing values, seasonality, censoring (detection limits) and serial dependence. Because the test is based on ranks, the advantage of the non-parametric tests over the parametric tests is that they are robust and more suitable for non-normally distributed data with missing and extreme values, frequently encountered in environmental time

series (De Leeuw, 2000; Holland et al., 2004; Sicard et al., 2009, 2011a,b). Based on annual data, seasonality presents no theoretical or computational obstacles to its application (Sicard, 2006). To estimate the trend, a consistent non-parametric estimator was suggested and modified by Sen (1968) including the possibility of ties in the time series. The Sen Method is little affected by errors within the data values and it is robust because insensitive to the "extreme" and missing values (Sicard et al., 2011a). In order to assess the sensitivity of the derived trends, we replaced an annual extreme value (i.e. outlier "heat wave" 2003) by a new annual average using a smoothing of previous data. We calculated the confidence interval at 99 and 95% and the test was used with four significance levels p: 0.1, 0.05, 0.01 and 0.001.

In order to compare the annual trends in urban and rural stations, with similar geographical location and characteristics, we selected 32 coupled stations for which both typologies are available within a radius of 50 km around the station. For each station, the annual data (average, 98th percentiles and hourly peak ozone concentrations) and the mean deviation are calculated from hourly data in both stations and the associated trends are obtained over the period 2000–2010.

2.3. Background pollution: mapping by co-kriging

The geographical distribution of background stations is rarely homogeneous and gaps can be noted. Spatial distributions were developed within the ArcGIS 9.2 software (Environmental Systems Research Institute) and its extension Geostatistical Analyst. The rural monitoring stations, representative of background ozone pollution, were georeferenced and interpolation maps were produced by assuming that surface ozone data at the rural stations are representative for a radius of 100 km around a station (De Leeuw et al., 2000). Secondly, ordinary co-kriging on station data and GTOPO30 DEM, for taking into account topographic effects, were carried out and provided the best estimate of the interpolated value. GTOPO30 is a global digital elevation model (DEM) with a horizontal grid spacing of approximately 1 km. GTOPO30 was derived from several raster and vector sources of topographic information. The co-kriging was performed with a Gaussian semivariogram model with 10 lags, 0.1 lag size, without anisotropy and second order of trend removal for station data. For ozone dataset, the geographical distribution of monitoring stations was heterogeneous; then, the interpolation was defined and carried out using 4 nearby stations (neighbors) with a minimum of 1 neighbor. For topography dataset DEM, the geographical distribution was homogenous (regular grids), thus, the co-interpolation, used more neighbors (24 with a minimum of 2). Applying kriging allowed creation of a continuous information layer from a set of individual sample points, except in North Sardinia, Sicily and Corsica. Layers were developed for annual data and associated trends: daily and hourly maxima, 24-h mean, median and 98th percentile of ozone concentrations. The parameterization of co-kriging was made thanks to prediction errors, based on the measured and predicted values, such as Mean Standardized (MS) and Root Mean Square Standardized Error (RMSSE), of the surface outputs from co-kriging for the whole domain (Table 1).

3. Results

The statistics for rural, urban and suburban sites are shown separately in order to present the trend magnitude for each typology. For mapping, background pollution maps were produced by co-kriging of surface ozone data in rural stations. Inversely, suburban and urban stations, representative of local conditions, were superimposed with colored symbols representing the value at each site.

3.1. Geographical distribution

The co-kriging was able to compensate for the lack of sufficient sampling in some areas. The RMSSE was always close to 1 (Table 1), with 1 highlighting no variability in prediction and thus no uncertainty for the whole domain. When predictions tend to underestimate the variability, RMSSE is more than 1. The MS error was near zero, suggesting the predictions were unbiased, i.e. centred on the true values. The best predictions were obtained for 24-h mean concentrations, as well as, for annual trends of mean and median concentrations and P98 in rural stations.

At rural stations, the ozone mean concentrations (Table 2) ranged from 42.5 (Milan, North Italy) to 99.5 μg m^{-3} (Gozo, Malta). Largely due to the high altitude of the stations, relatively high concentrations, > 80 μg m^{-3}, were found in Sierra Nevada (South Spain), Pyrenees (Southwestern France), Alps (Italian-French border), Apennine mountains (inland Italy) and a hot spot close to the border with Austria in North-eastern Italy (Fig. 1). The lowest mean concentrations, < 50 μg m^{-3}, were observed at low altitude stations along the Po valley. The lowest maxima and P98 (<120 μg m^{-3}) were observed in South Sardinia and Spain, particularly Balearic Islands, and relatively high 98th percentiles (>150 μg m^{-3}) and hourly maxima (>200 μg m^{-3}) were found in North and Central Italy and South-eastern France (Figs. 2 and 3). At urban and suburban sites, the ozone mean concentrations (Table 2) ranged from 34.1 (Milan, North Italy) to 95.3 μg m^{-3} in South-eastern France, at Grasse, where NMVOC emissions increased till 2007 because of the installation of perfumery and industrial chemistry factories (Directive 96/61/CE). The highest concentrations (>65 μg m^{-3}) were found in South Spain, South Italy (Sicily) and South-eastern France (Fig. 1). The lowest mean concentrations (<45 μg m^{-3}) were observed in North Italy which is well-industrialized. The higher P98 (>150 μg m^{-3}) and maxima (>200 μg m^{-3}) were in large cities such as those in South-eastern France (Marseille), North Italy (Milan) and Rome, and the lowest P98 and maxima (<110 μg m^{-3}) were in South Spain and South Sardinia (Figs. 2 and 3).

3.2. Changes in ozone concentrations over time

Over the period 2000–2010, annual mean concentrations significantly decreased by 0.43% $year^{-1}$ at rural sites (Table 2). Negative trends were observed for P98 (−0.90% $year^{-1}$), daily (−0.81% $year^{-1}$) and hourly maxima (−1.21% $year^{-1}$). Urban stations increased annual mean concentrations by 0.64% $year^{-1}$ and median values by 1.21% $year^{-1}$. P98 (−0.74% $year^{-1}$), daily (−0.54% $year^{-1}$) and hourly maxima (−1.25% $year^{-1}$) decreased over time. Suburban stations increased annual averages (+0.46% $year^{-1}$) and median values (+0.98% $year^{-1}$), and decreased P98 (−0.67% $year^{-1}$), daily (−0.92% $year^{-1}$) and hourly maxima (−0.96% $year^{-1}$).

Table 1
Prediction errors (Mean Standardized *MS* and Root Mean Square Standardized Error *RMSSE*) of the surface outputs from co-kriging for annual average, median, 98th percentile and hourly maximum (in μg m^{-3}) and associated trend values (% $year^{-1}$) over the period 2000–2010 in rural stations for the whole domain.

	MS	RMSSE
Mean	−0.006	1.007
Trend	−0.002	0.996
Median	−0.092	1.018
Trend	−0.007	1.007
P98	−0.051	0.982
Trend	−0.001	0.972
Hourly max	−0.021	1.034
Trend	0.013	1.030

Table 2
Statistics and annual trends (average, minimum and maximum) for annual ozone average, median, 98th percentile (P98), hourly and daily maxima obtained by the Mann–Kendall test over the period 2000–2010.

	Rural sites			Suburban sites			Urban sites		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
Mean (μg m^{-3})	66.2 ± 5.4	42.5	99.5	57.3 ± 5.2	36.1	95.3	52.0 ± 5.1	34.1	66.7
Trend (% yr^{-1})	−0.43	−3.63	+4.98	+0.46	−3.44	+4.91	+0.64	−3.49	+5.22
Median (μg m^{-3})	63.5 ± 5.4	27.1	98.6	54.1 ± 5.6	23.4	90.55	47.8 ± 5.2	17.0	66.4
Trend (% yr^{-1})	+0.01	−4.88	+9.45	+0.98	−6.67	+6.90	+1.21	−2.54	+7.37
P98 (μg m^{-3})	134.3 ± 11.7	109.0	186.7	131.9 ± 10.8	106.0	171.9	130.4 ± 12.6	98.3	160.8
Trend (% yr^{-1})	−0.90	−3.33	+2.50	−0.67	−2.87	+1.55	−0.74	−5.01	+5.52
Hourly max (μg m^{-3})	189.1 ± 22.2	135.3	321.0	192.2 ± 24.6	142.8	272.2	190.4 ± 26.0	128.2	270.9
Trend (% yr^{-1})	−1.21	−3.82	+3.31	−0.96	−3.02	+1.86	−1.25	−5.32	+2.94
Daily max (μg m^{-3})	125.4 ± 12.9	96.4	177.8	118.2 ± 11.8	92.0	172.3	116.4 ± 14.2	83.0	153.6
Trend (% yr^{-1})	−0.81	−3.63	+4.55	−0.92	−4.37	+2.58	−0.54	−3.23	+7.20

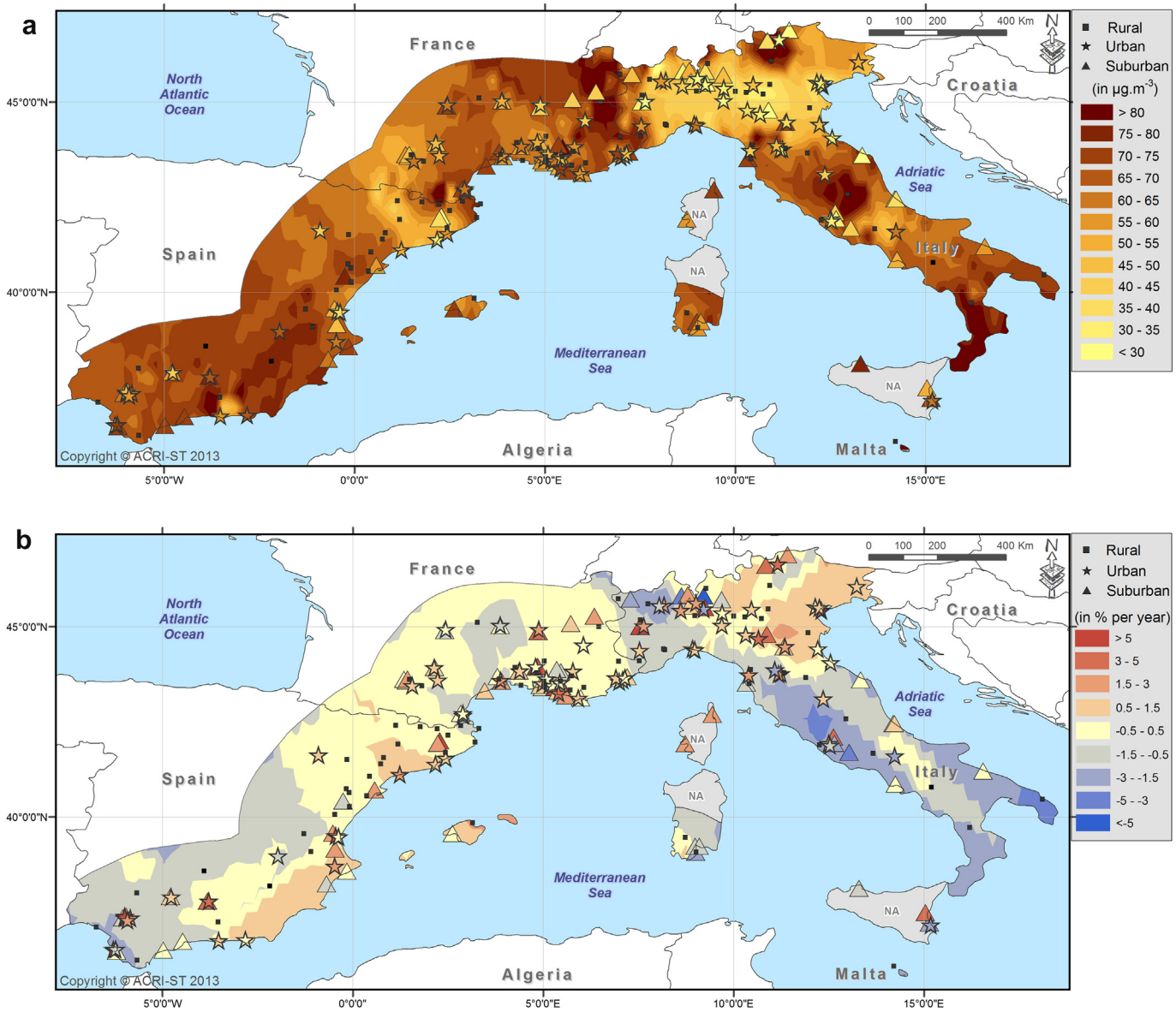

Fig. 1. Ozone annual averages (up) and annual trends (down) based on 66 rural stations, representative of the background pollution, and in 73 urban and 74 nearby suburban stations over the time period 2000–2010 (NA: not applicable).

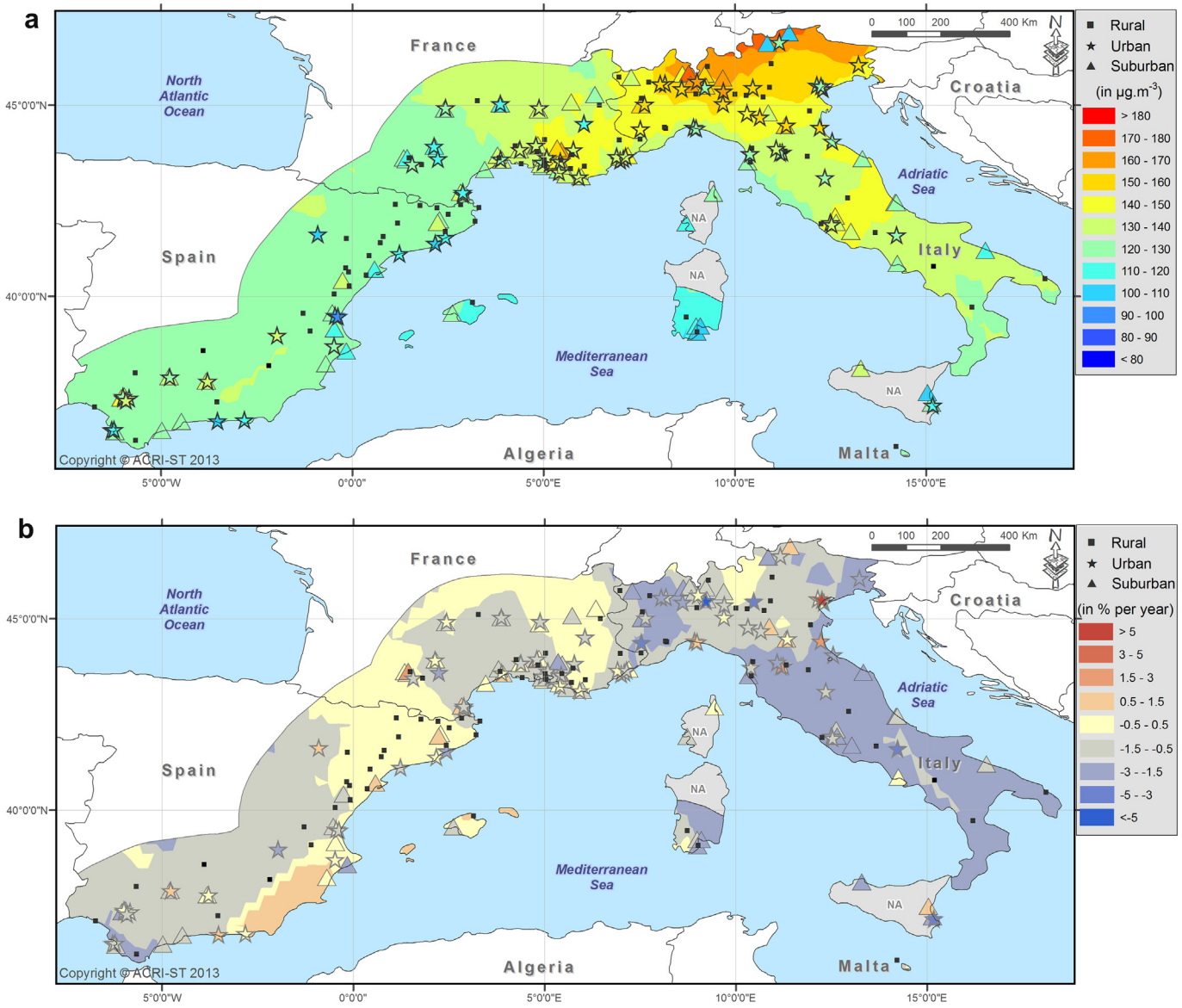

Fig. 2. 98th percentiles (up) and annual trends (down) based on 66 rural stations and in 73 urban and 74 nearby suburban stations over the time period 2000–2010 (NA: not applicable).

For annual mean concentrations, 58.2% of rural stations showed a decrease over time. P98 and maxima decreased at 77.6% and >79% of rural sites, respectively (Table 3). For the annual averages and maxima, the most significant increases (>+2.0% year^{-1}) were in North-eastern Italy, North Adriatic Sea, in South-eastern Spain (Sierra Nevada Mountains) and Balearic Islands (Figs. 1–3). A stable trend was observed in North-eastern Spain and France along the coastline. For all metrics, the most significant negative annual trends (<−3.0% year^{-1}) occurred across Italy, except North Adriatic Sea, with hot spots around Rome and the very South of Italy (Figs. 1–3).

For mean concentrations, 64.4% and 60.8% of urban and suburban stations, respectively, showed an increase. The increase was significant in Spain and France (Table 3). In contrast, suburban sites in Italy showed a tendency to decrease. The most significant decreases (<−1.5% year^{-1}) were in Sicily and Central Italy and important increases (>+3.0% year^{-1}) were in South Spain (Andalusia) and North-eastern Italy (Fig. 1). Negative annual trends in P98 and hourly maxima were observed at >75.0% of urban and 71% of suburban stations, particularly in France. The most significant decreases for P98 and maxima (−3.0% year^{-1}) were in the Italian Alps and Rome area (Figs. 2 and 3). For P98, increases (>+1.5% year^{-1}) were observed in North Adriatic Sea. Negative trends (<−1.5% year^{-1}) were observed in France, Sierra Nevada Mountains, Balearic Islands and Northern part Italy with significant trends (<−3.0% year^{-1}) in Central Italy and Italian Alps. For hourly maxima, significant negative trends (<−3.0% year^{-1}) occurred around Rome, in Alps, South Sardinia and Spain (Valencia region).

Using a robust statistical test, we assessed the sensitivity of the derived trends, to the years included in the decadal average showed that the magnitude trend for annual averages, median and peaks were slightly (±0.05%) weighted by the 2003 European "heat wave" year.

3.3. Changes in ozone precursors emission over time

Around the Mediterranean basin, over the period 2000–2010, significant decreasing trends of NO_x, Non-Methane-Volatile-

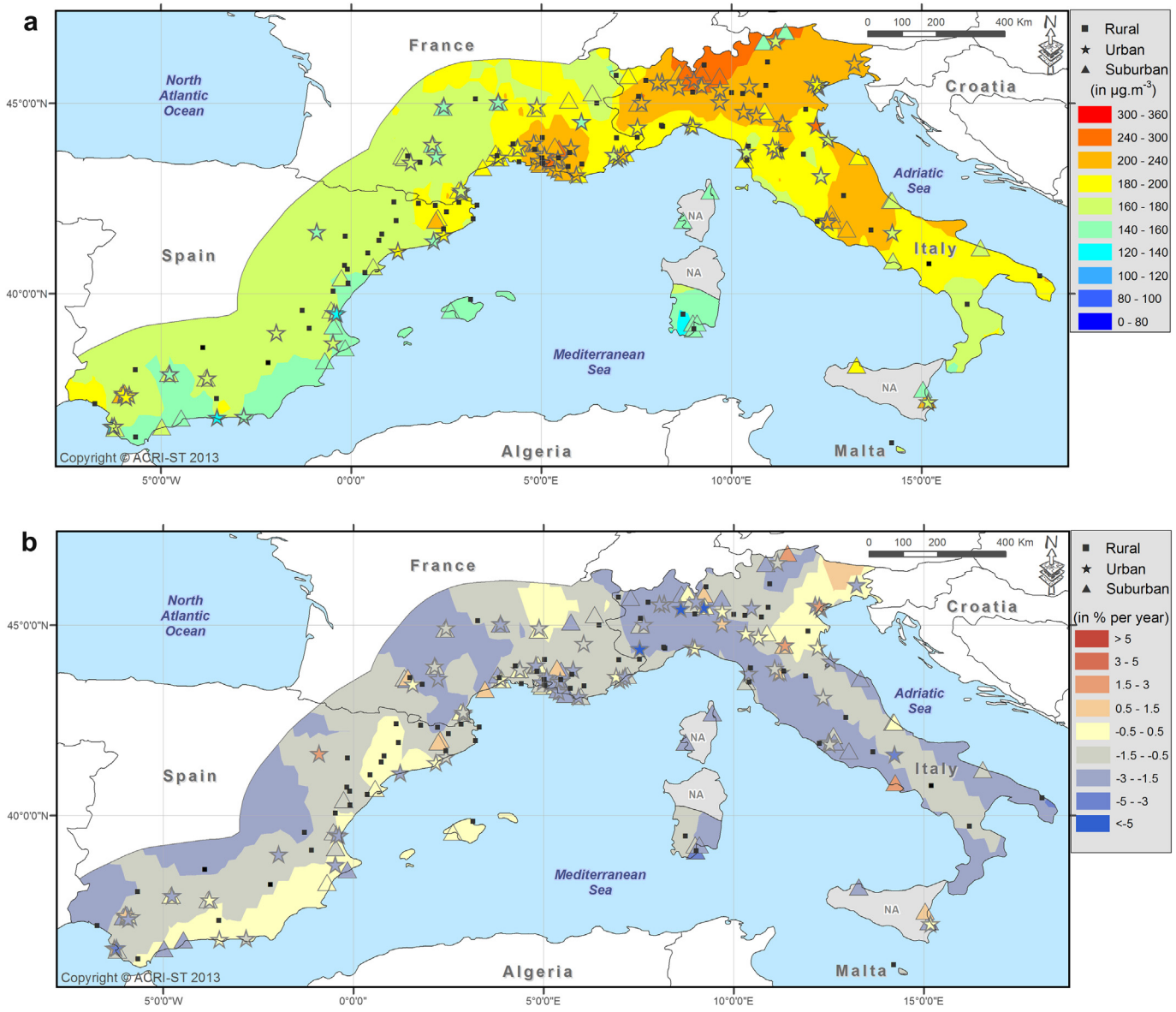

Fig. 3. Hourly maxima ozone concentrations (up) and annual trends (down) based on 66 rural stations and in 73 urban and 74 nearby suburban stations over the time period 2000–2010 (NA: not applicable).

Organic-Compounds NMVOC and CO emissions were recorded (Table 4), except in South-eastern Europe, such as Croatia, Greece and Serbia. In Turkey, emissions have increased for CO and NO_x, and have slight decreased for NMVOC. Over the period 1990–2010, significant increasing trends for NO_x emission were recorded, such as in Croatia, Greece, Spain and Cyprus. For NMVOC, an increase in Albania and Croatia, no change in Montenegro, and decreases in the other countries were recorded. The majority of Europe showed negative trends in CO, NO_x and NMVOC emissions from 1990 and particularly from 2000.

4. Discussion

4.1. Distribution over the period 2000–2010

Surface ozone concentrations in the South-western European Mediterranean Basin were relatively high (Fig. 1) relative to human well-being (WHO, 2008) and vegetation impacts (Sanz and Millan, 2000; Paoletti, 2006). High annual mean ozone concentrations, exceeding 80 µg m^{-3}, were recorded in some regions and, particularly, along the coasts, because of shipping tracks (Konovalov et al., 2008), industrial development, road traffic increment, high insolation and sea/land breeze recirculation (Millan et al., 2000; Alonso et al., 2001; Vestreng et al., 2009). The annual average background ozone concentrations, over the mid-latitudes of the Northern Hemisphere, range between approximately 40–90 µg m^{-3} (Vingarzan, 2004). The annual ozone levels at Canadian background stations fall between 46 and 68 µg m^{-3}, similar to that reported for low elevation background stations in North America and the United States (Vingarzan, 2004). Simulations indicated mean North American and U.S. background concentrations of 50–60 µg m^{-3} at remote U.S. sites in 2001 (Wang et al., 2009).

In the Mediterranean, ozone precursor emission and insolation are usually high, especially during summertime (Paoletti, 2006; Kalabokas et al., 2008; Giannakopoulos et al., 2009; Lelieveld et al., 2002; Velchev et al., 2011). Lelieveld et al. (2002) found that summer ozone concentrations over the Mediterranean were 2.5–3 times higher than in the background troposphere. In

Table 3
Number of stations per annual trend category (decrease, increase and no change) for annual ozone average, median, 98th percentile (P98), hourly and daily maxima obtained by the Mann–Kendall test over the period 2000–2010 in France (FR), Spain (ES), Malta (MT) and Italy (IT).

	Rural sites					Suburban sites				Urban sites			
	ES	FR	IT	MT	%	ES	FR	IT	%	ES	FR	IT	%
Mean													
Increase	12	8	8	0	**41.8**	11	24	10	**60.8**	15	15	17	**64.4**
No change	0	0	0	0	**0**	0	0	0	**0**	0	0	0	**0**
Decrease	13	9	16	1	**58.2**	5	7	17	**39.2**	3	9	14	**35.6**
Median													
Increase	12	6	8	0	**38.8**	11	23	12	**62.2**	16	18	22	**76.7**
No change	2	7	0	0	**13.4**	2	3	2	**9.5**	0	3	3	**8.2**
Decrease	11	4	16	1	**47.8**	3	5	13	**28.4**	2	3	6	**15.1**
P98													
Increase	7	2	3	0	**17.9**	4	8	4	**21.6**	4	3	9	**21.9**
No change	2	1	0	0	**4.5**	0	2	0	**2.7**	1	1	0	**2.7**
Decrease	16	14	21	1	**77.6**	12	21	23	**75.7**	13	20	22	**75.3**
Hourly max													
Increase	7	1	2	0	**14.9**	2	6	8	**21.6**	5	0	10	**20.5**
No change	0	0	1	0	**1.5**	0	2	0	**2.7**	1	1	0	**2.7**
Decrease	18	16	21	1	**83.6**	14	23	19	**75.7**	12	23	21	**76.7**
Daily max													
Increase	8	1	5	0	**20.9**	6	13	2	**28.4**	9	3	10	**30.1**
No change	0	0	0	0	**0**	0	0	0	**0**	0	1	0	**1.4**
Decrease	17	16	19	1	**79.1**	10	18	25	**71.6**	9	20	21	**68.5**

summer, the western part of the Mediterranean basin is dominated by high pressure and thus atmospheric stability under the descending branch of the Hadley circulation and the influence of weak levels of Azores anti-cyclonic subsidence (Velchev et al., 2011). These conditions favor massive photochemical processes and emissions of biogenic volatile organic compounds to the atmosphere and thus the production of O_3 (Millan, 2002; Lelieveld, 2009; Giannakopoulos et al., 2009). Georgiadis et al. (1994) and Jiménez et al. (2006) showed that the complex layout of coasts and surrounding mountains favors the development of combined sea breezes. At night, land breezes can store polluted air masses above the maritime boundary layer and thus build reservoirs of polluted air that may return onshore on the following day (Ancellet and Ravetta, 2005). A residual-layer is present near the coast and the influence of ozone conservation in the nocturnal residual layer, on the development of the near surface ozone concentration of the next day, was studied. The rapid rise of ozone in the morning is due to a combination of photochemical processes and residual layer re-entrainment (Kulkarni et al., 2011; Sousa et al., 2011; Hu et al., 2013). Based on observational and modeled data, Lelieveld et al. (2002) suggested that the long range transport of European polluted air toward the Mediterranean Basin is an important cause of elevated ozone levels in the Western Mediterranean area.

As expected, the highest annual averages were observed (Fig. 1) at rural stations and high altitude stations (>95 μg m^{-3}). Altitude reduces the ozone destruction by deposition (Saavedra et al., 2012), and increases the input of stratospheric ozone (Fusco and Logan, 2003; Derwent et al., 2004) and solar radiation. Biogenic VOC emission, low ozone titration by NO pollution, and ozone and/or precursors transport from urban areas are known factors to explain higher ozone pollution at rural sites than in the cities (De Leeuw, 2000; Sicard, 2006). High ozone averages have been reported in rural stations across Italy and Eastern Spain (Millan et al., 2000; Kalabokas and Repapis, 2004; Paoletti, 2006). The high ozone levels observed at the island of Gozo (Malta) are confirmed by Velchev et al. (2011) and Nolle et al. (2002) showing a maximum value approximately twice as high as on the European continent. The lowest annual averages (<50 μg m^{-3}) were at low altitude stations, along the Po valley, possibly due to a strong influence of urban areas. The highest P98 were at rural stations (Fig. 2) while the highest hourly maxima were in the cities (Fig. 3). The ozone concentrations over the Western European Mediterranean basin are significantly higher than for the rest of Europe (e.g. Jonson et al., 2001).

4.2. Trends in urban/suburban and rural stations

The background level increased by $+0.64\%$ year^{-1} and $+0.46\%$ year^{-1}, respectively at urban and suburban stations (Table 3), and slightly decreased (-0.43% year^{-1}) at rural stations. A significant reduction in the peak ozone concentrations occurred at all stations (Table 4). Indeed, P98 decreased at more than 75% of stations (-0.77% year^{-1}) and annual peaks at more than 76% of stations (-1.14% year^{-1}). Other studies covering global European trends from 1990 showed no change or a slight increase and significant reductions in P98 and annual peaks (De Leeuw, 2000; Sicard et al., 2009; Saavedra et al., 2012; Wilson et al., 2012). Potential reasons for the observed ozone trends have been discussed by several authors (Derwent et al., 1998; Szopa et al., 2006; Jonson et al., 2006; Sicard et al., 2011a; Wilson et al., 2012).

From the comparison of 32 coupled stations, higher ozone concentrations were measured in rural areas than in the nearby urban stations with "rural/urban" ratios ranging from 1.1 to 1.5 (Table 5). Still, a significant decrease of annual average occurred at rural stations (-1.5% year^{-1}) while the cities showed an increase (Table 5). In contrast, the peak ozone concentrations, e.g. P98 and hourly peaks, showed a similar decline at rural and urban sites. In the cities, background ozone levels increased but peak ozone concentrations decreased (Table 3). This is in agreement with other studies in United Kingdom, United States and France (Coyle et al., 2003; EPA, 2006; Sicard et al., 2011a). The increase in annual mean concentrations can be attributed to a reduced titration of ozone, by reaction with NO, in response to a reduction in NO_x emissions (Table 4) e.g. due to a reduction of road traffic (Vestreng et al., 2008). The reduction in rural stations, representative of background pollution, can be attributed to the reduction in NO_x and VOC emissions within the European Union (Table 4). With the exception of Spain and North-eastern Italy, where positive trends in annual mean and P98, were observed (Figs. 1 and 3).

It is recognized that ozone values in the middle of the frequency distribution (e.g. median) are less sensitive to emission changes than ozone values at the high end of the frequency distribution, e.g.

Table 4
National annual emissions (Gg) and trends (% year^{-1}) of the ozone precursors non-methane volatile organic compounds (NMVOC), nitrogen oxides (NO_x = NO + NO_2) and carbon monoxide (CO) obtained by the Mann–Kendall test over the time periods 1990–2010 and 2000–2010.

	2000–2010						1990–2010					
	NMVOC		NO_x		CO		NMVOC		NO_x		CO	
	Mean (Gg)	% year^{-1}	Mean (Gg)	%.year^{-1}	Mean (Gg)	% year^{-1}	Mean (Gg)	% year^{-1}	Mean (Gg)	% year^{-1}	Mean (Gg)	% year^{-1}
Albania	29.4 ± 3.9	+9.3*	22.0 ± 2.5	+5.1*	127.2 ± 27.3	+6.6	30.0 ± 6.0	+0.7*	19.8 ± 3.4	+2.8**	129.9 ± 30.9	−1.0+
Bulgaria	87.1 ± 2.9	+0.4	138.1 ± 14.0	−0.7	327.1 ± 40.9	−2.1*	185.1 ± 182.1	−3.5***	147.5 ± 27.2	−1.1***	409.5 ± 111.2	−2.7***
Croatia	93.5 ± 13.5	+5.4	78.3 ± 4.9	+1.8	347.7 ± 51.7	−2.8***	90.0 ± 13.1	+1.5**	75.0 ± 8.4	+1.8**	383.6 ± 68.5	−1.7**
Cyprus	13.5 ± 1.2	−1.8**	20.7 ± 1.1	−0.9**	27.3 ± 5.5	−3.2***	14.8 ± 1.7	−1.5***	20.0 ± 1.4	+0.8+	36.2 ± 10.9	−3.3***
E.Union (27)	8848 ± 1074	−2.3***	11,227 ± 1207	−1.8***	30,850 ± 5041	−2.9***	11,279 ± 2957	−3.0***	13,068 ± 2350	−2.3***	41,941 ± 13,545	−3.4***
France	1240 ± 300	−3.5***	1374 ± 184	−2.4***	5165 ± 957	−3.0***	1718 ± 589	−3.6***	1561 ± 248	−1.9***	7155 ± 2425	−3.6***
Greece	233.2 ± 24.2	−1.9***	388.6 ± 28.0	+0.4	744.8 ± 131.0	−2.9***	248.1 ± 23.7	−1.0***	368.5 ± 30.8	+1.4***	875.6 ± 176.1	−2.4***
Italy	1329 ± 164	−2.4***	1204 ± 162	−2.5***	3596 ± 729	−3.2***	1661 ± 384	−2.6***	1523 ± 385	−2.9***	5135 ± 1798	−3.5***
Malta	3.1 ± 0.3	−1.0	9.1 ± 0.5	−0.6	4.4 ± 7.3	+7.3***	na[b]	–	na	–	na	–
Monaco	0.4 ± 0.1	−2.8***	0.4 ± 0.1	−2.0***	1.4 ± 0.3	−3.2**	0.6 ± 0.2	−3.4***	0.4 ± 0.1	−2.5***	2.1 ± 0.8	−3.8***
Montenegro	9.1 ± 0.7	+0.3	8.0 ± 0.8	+1.6+	35.3 ± 5.2	−2.1**	9.1 ± 1.0	0*	7.3 ± 1.7	+1.7*	38.8 ± 10.3	−1.7*
Serbia	130.3 ± 5.2	+1.0+	179.7 ± 18.4	+6.0***	415.1 ± 44.8	+4.9**	na	–	na	–	na	–
Slovenia	40.2 ± 4.3	−2.2***	48.7 ± 2.5	−1.0*	180.6 ± 21.5	−2.3***	47.7 ± 9.1	−2.3***	52.6 ± 5.2	−1.1***	234.3 ± 64.4	−2.9***
Spain	841.1 ± 99.3	−2.3***	1290 ± 152	−1.6*	2201 ± 325	−2.6***	925.4 ± 116.6	−1.6***	1307 ± 111	+0.2+	2752 ± 673	−2.8***
Turkey	633.8 ± 144.6	−0.03	796.1 ± 115.6	+1.4	3892 ± 228	+19.1	na	–	na	–	na	–
FYRM[a]	28.8 ± 7.1	+0.1	35.0 ± 5.8	−0.9	93.8 ± 18.6	+0.6	na	–	na	–	na	–

Significance level p = 0.001***, 0.01**, 0.05*, 0.1. ± is the standard deviation.
[a] FYRM: The Former Yugoslav Republic of Macedonia.
[b] na: no available data.

Table 5
Annual averages, hourly maxima, 98th percentiles, standard deviations and associated annual trends obtained for 32 rural/urban coupled stations over the time period 2000–2010.

	Rural sites	Urban sites
Mean (μg m^{-3})	64.5 ± 7.1	51.8 ± 12.2
Trend (% yr^{-1})	−1.5	+0.3
P98 (μg m^{-3})	144.7 ± 11.6	142.2 ± 13.4
Trend (% yr^{-1})	−1.3	−1.2
Hourly max (μg m^{-3})	220.1 ± 25.8	217.7 ± 18.2
Trend (% yr^{-1})	−1.6	−1.9

P98 (De Leeuw, 2000). At more than 75% of stations, the significant reduction in P98 and peak ozone concentrations (Table 2) might largely be attributed to the substantial decreases in the ozone precursor's emissions within the European Union which started in the early 1990, particularly in South of France and Italy (Table 4). In Western Europe, the introduction of improved vehicle technologies and stringent inspection systems related to the Euro standards[1] has been the primary force in reducing NO_x road traffic emissions from 1990, despite economic growth and increases in fuel consumption (Vestreng et al., 2008; Monks et al., 2009). In addition, the decrease of NMVOC emissions can be attributed to the progressive consequences of the vehicles equipment into catalytic exhaust pipes and the progress in the storage and distribution of hydrocarbons. The most significant reductions (>−3.0% year^{-1}) in peak ozone values were in urban and suburban areas (Fig. 3). The benefit of both global and European emission control measures is a significant decrease of peak ozone concentrations and extreme episodes.

Between 2000 and 2010, the NMVOC and NO_x emissions have increased over the countries of the Eastern Mediterranean basin (Table 4) likely because the Euro standards were not applied as in the rest of Europe (Vestreng et al., 2008). Furthermore, NO_x emissions have significantly increased between 1990 and 2010 over countries of the Eastern Mediterranean basin (e.g. Vestreng et al., 2008) and Spain resulting in an observed slight increase in ozone (Fig. 1). The high age of the vehicle fleet combined with increasing number of vehicles may contribute to the lack of reductions in Spain. These differences in the ozone trends between the South of the Iberian Peninsula and the rest of Europe can be explained because of the increment of emissions from 1990 to 2010.

Trends in NO_x and VOC emissions showed near uniform decrease in ozone precursor emissions across the southwestern Europe (apart from increases in NO_x in Spain) likely due to National and European legislation over the past 20 years, and the modernization or removal of industrial sources. A modeling study by Szopa et al. (2006), showed the positive impact of emission control measures, undertaken by some countries, on the decrease of extreme ozone exposure episodes in Europe. In a model experiment reducing the anthropogenic emissions stepwise in Europe (Monks et al., 2003) it was demonstrated that the largest effects on mean ozone was seen when removing the last 15–20% of the ozone precursor emissions. Thus reductions in surface ozone caused by more moderate reductions in ozone precursors could easily be masked by inter-annual variability and/or a trend in background ozone (e.g. Wang et al., 2009).

Additional reasons, suggested by authors, can explain the observed trends. The peak ozone concentrations may be determined not only by long-range transport of ozone and its precursors

[1] European emission standards define the acceptable limits for exhaust emissions (including NO_x, non-methane hydrocarbons, CO and particulate matter) of new vehicles sold in EU member states – http://eur-lex.europa.eu.

but also by local emissions of precursors (Elichegaray et al., 2002). Some studies have indicated that intercontinental transport appears to be an important factor that may explain observed ozone trends (Derwent et al., 1998; Szopa et al., 2006; Sicard, 2006). Models have shown that the benefit of European emission control measures can be significantly counterbalanced by increasing background ozone levels and subsequent long range transport (Szopa et al., 2006; Derwent et al., 2010). *In fine*, the observed slight increase in surface ozone concentrations can be attributed to precursor's emissions increase from the Eastern Mediterranean basin. As an additional factor, not yet quantified, climate change and local meteorological conditions can move these trends to either positive or negative (Amann et al., 2008; Sicard et al., 2012), as well as, the influence of stratospheric–tropospheric ozone exchange, mainly in the high-lying stations (Fusco and Logan, 2003), and the exchange between the free troposphere and the boundary layer (Kulkarni et al., 2011; Hu et al., 2013).

5. Conclusions

The implementation of decided emission control legislation in the individual countries worldwide leads to a geographically heterogeneous impact on surface ozone levels over Europe. At background sites over the time period 2000–2010, we demonstrated for the first time that the ozone control measures are effective at rural sites, while ozone concentrations are still increasing in the cities. This result is challenging the traditional knowledge about ozone pollution as a minor air quality issue in urban atmospheres. The establishment of temporal ozone trends is important for quantifying the impact of changing precursor emissions and also from the perspective of local and regional air quality control.

A marked spatial variability of the trends was observed and could reflect the effect of the 2003 heat wave (Vautard et al., 2005). Ozone production is strongly influenced by the meteorological conditions (Elichegaray et al., 2002), thus, in order to better assess the influence of emission changes on the observed ozone, a robust statistical test is required to remove the influence of the meteorological variability. The derived magnitude trends were slightly weighted by the European "heat wave" in 2003. The study suggests that the Mann–Kendall approach is scientifically-sound and is a useful tool for an analysis of ozone and ozone precursor's trends in the Mediterranean Europe and for an associated risk assessment. The test is suitable for non-normally distributed data with missing and extreme values, frequently encountered in environmental time series.

Results confirm that the Western Mediterranean region is characterized by photochemical episodes and high background ozone concentrations in both urban and remote areas. The results showed a convergence of ozone pollution at remote and urban sites in the Mediterranean Europe. Despite a significant decrease of ozone precursor's emissions over the Western part of the European Mediterranean basin, we observed an average increments (+0.64% per year) in urban stations and an average decrease (−0.43% per year) in rural stations. This situation with respect to near-surface ozone in rural areas is comparable to the one observed in other countries (Canada, Germany, Ireland and Switzerland).

There is good evidence for an increase in the global background level of ozone over the past few decades in urban areas. Urban ozone concentrations are expected to rise over the next decades and to tend towards the concentrations found in the rural areas that surround them. At cities background ozone levels increased but peak ozone concentrations decreased. These increases in urban ozone concentrations are likely driven by vehicle emission controls that have brought about a reduction in nitrogen oxides (NO_x) emissions in urban areas. Urban ozone concentrations will also respond to the changes occurring to ozone in the surrounding rural areas, largely driven by changes on the hemispheric/global scale. At urban stations, the paradox which shows an increase in surface O_3 concentrations associated with a reduction of precursor emissions over Europe is highlighted. In contrast to the reported increase in the ozone mean values or related statistics, we observed a significant decrease in the upper percentiles of the ozone distribution function. Thus, the ozone pollution appears as a major air quality issue in urban areas and we need an assessment of the ozone effects on urban trees, health and well-being of citizens to define suitable city planning. To define appropriated thresholds for protection against ozone pollution, additional specific analyses of ozone symptoms/impacts and real damage levels in the field are needed. These results will serve as a decision-support tool for National and European authorities. With information in hand, policymakers can make informed decisions about proposed changes to legislation to scientifically assess the effectiveness of air pollution control strategies in European urban areas. Future EU urban monitoring is needed to improve our knowledge and to quantify as reliably as possible any changes that are taking place. In urban locations, the combination of sources (trends in background ozone, climate change and reductions in the NO_x titration effect) must be reflected in air quality strategies aimed at improving air quality in urban locations.

A number of sites affected by urban pollution have been reporting declining trends, and at the same time other studies are reporting increasing trends. Some of the reasons for this uncertainty stem from the relatively small number of background stations, and reflects the influence of local pollution.

In urban areas, ground-level ozone can become an increase sanitary problem affecting trees, biodiversity and well-being of citizens. The ground-level ozone affects urban trees through visible leaf symptoms (Paoletti et al., 2009a,b; Sicard et al., 2011a), decreasing foliar chlorophyll content (Dalstein et al., 2002, 2005), accelerating leaf senescence (Pell et al., 1999; Gielen et al., 2007), decreasing photosynthesis (Coleman et al., 1995a,b), decreasing carbon sequestration (Coleman et al., 1995a,b; Büker et al., 2012), predisposing to pests attack (Manning and von Tiedemann, 1995; Karnosky et al., 2002) and decreasing growth and productivity (Karnosky et al., 2007; Mills et al., 2011) and a variety of other physiological effects in plants (Karnosky et al., 2007). Furthermore, extensive research (Katsouyanni et al., 1995; WHO, 2000, 2008; Kassomenos et al., 2008; Sicard et al., 2011b) has demonstrated the associations between surface ozone and ill-health endpoints such as increased hospital admissions for respiratory, cardiovascular disease and congestive heart failure, increases in asthma attacks, increases in acute bronchitis and decreased lung function. Ozone can enter the body through inhalation and can reach the respiratory system. Acute exposure to high ozone levels can induce changes in lung function, airway inflammation and increased airway responsiveness to broncho-constrictors. Ozone exposure has also been associated with increased numbers of hospital admissions from respiratory diseases, including asthma (Kassomenos et al., 2008; Sicard et al., 2011b).

Climate change is projected to reduce the benefits of ozone precursor emissions controls and will need to be factored into future ozone policies. Climate models predict that Mediterranean summers will be increasingly characterized by warm, dry weather with calm winds (IPCC, 2001). Thus the conditions, that favor high ozone levels, will be likely more frequent in the future. In conclusion, much work remains to be done in the characterization of regional and global surface ozone trends. Long term monitoring is needed to establish the actual trends in air pollution over the Western European Mediterranean region. The continued collection of data at background stations is of critical importance in this work.

Ozone and climate change are interlinked, thus, the development of coordinated emission reduction strategies are useful to reduce both climate change and ozone pollution.

Acknowledgments

This work was made possible with the contribution of the LIFE financial instrument of the European Union (LIFE10 ENV/FR/208) and the French Minister for Agriculture, Food, Fisheries, Rural Affairs and Town and Country Planning (MAAPRAT) and thanks to the good cooperation and harmony between the project partners: ACRI-ST, GIEFS, IPP-CNR and ENEA. This work was made possible by the technical support of the European Environment Agency (EEA) with the access to the European Air quality database AirBase.

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