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Particulate matter and gaseous pollutants in the Mediterranean Basin: Results from the MED-PARTICLES project

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HIGHLIGHTS

- The air pollutant long-term trends revealed significant decrease for PM, SO_2 and CO
- For NO_2 no clear trend or slightly increasing trends were observed
- The coarse fraction, $PM_{2.5-10}$ is important in the Mediterranean Basin
- The origin of air pollution in southern Europe is rather local than regional

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ABSTRACT

Previous studies reported significant variability of air pollutants across Europe with the lowest concentrations generally found in Northern Europe and the highest in Southern European countries. Within the MED-PARTICLES project the spatial and temporal variations of long-term PM and gaseous pollutants data were investigated in traffic and urban background sites across Southern Europe. The highest PM levels were observed in Greece and Italy (Athens, Thessaloniki, Turin and Rome) while all traffic sites showed high NO_2 levels, frequently exceeding the established limit value. High $PM_{2.5}/PM_{10}$ ratios were calculated indicating that fine particles comprise a large fraction of PM_{10}, with the highest values found in the urban background sites. It seems that although in traffic sites the concentrations of both $PM_{2.5}$ and PM_{10} are significantly higher than those registered in urban background sites, the coarse fraction $PM_{2.5-10}$ is more important at the traffic sites. This fact is probably due to the high levels of resuspended road dust in sites highly affected by traffic, a phenomenon particularly relevant for Mediterranean countries. The long-term trends of air pollutants revealed a significant decrease of the concentration levels for PM, SO_2 and CO while for NO_2 no clear trend or slightly increasing trends were observed. This reduction could be attributed to the effectiveness of abatement measures and strategies and also to meteorological conditions and to the economic crisis that affected Southern Europe.

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Table 1
Characteristics of the sampling sites used.

City	Site	Component	Latitude	Longitude	Station type	Sampling period	Missing data, %
Athens	Agia Paraskevi	PM_{10}, $PM_{2.5}$, NO_2, O_3	37°59′50N	23°49′0E	Suburban background	2007–2009	PM_{10}, $PM_{2.5}$: 2 O_3: 1 NO_2: 3
Athens	Patision	PM_{10}, SO_2, CO, O_3, NO_2	37°59′18N	23°43′40E	Traffic	2007–2009	PM_{10}: 8 SO_2: 7 O_3: 5 CO, NO_2: 3
Athens	Peiraias	PM_{10}, $PM_{2.5}$	37°57′28N	23°36′10E	Traffic	2007–2009	18
Barcelona	Palau Reial	PM_{10}, $PM_{2.5}$	41°23′14″N	2°06′56″E	Urban background–traffic influenced	2003–2010	10
Barcelona	Sant Gervasi	PM_{10}, $PM_{2.5}$, SO_2, CO, O_3, NO_2	41°24′1″N	2°08′5″E	Traffic	2004–2010	PM_{10}, $PM_{2.5}$: 6 SO_2, CO, O_3, NO_2, NO_x: 3
Barcelona	L'Hospitalet	SO_2, CO, O_3, NO_2, NO_x	41°21′35″N	2°06′4″E	Urban	2003–2010	SO_2, NO_2, NO_x: 12 CO, O_3: 8
Bologna	San Felice	PM_{10}, $PM_{2.5}$, CO, NO_2	44°30′0N	11°19′43E	Traffic	2006–2010	PM_{10}, $PM_{2.5}$: 6 CO: 9 NO_2: 8
Bologna	Giardini Margherita	NO_2, O_3	44°19′1N	11°21′18E	Urban background	2006–2010	NO_2: 19 O_3: 14
Huelva	Campus	PM_{10}, $PM_{2.5}$, SO_2, CO, O_3, NO_2, NO_x	37°15′57″N	6°55′26″W	Urban background–industry influenced	2003–2010	PM_{10}, $PM_{2.5}$, CO: 25 SO_2, NO_2, NO_x: 20 0_3: 14
Madrid	Pl. España	PM_{10}, SO_2, CO, O_3, NO_2, NO_x	40°25′26″N	3°42′44″W	Traffic	2001–2009	PM_{10}: 10 SO_2, CO, O_3, NO_2, NO_x: 3
Madrid	Cuatro Caminos	PM_{10}, $PM_{2.5}$, SO_2, CO, O_3, NO_2, NO_x	40°26′44″N	3°42′26″W	Traffic	2001–2009 for $PM_{2.5}$ 2004–2009	PM_{10}: 9 $PM_{2.5}$: 22 SO_2, CO, O_3, NO_2, NO_x: 4
Madrid	Casa de Campo	PM_{10}, $PM_{2.5}$	40°25′10″N	3°44′50″W	Urban background	2001–2009 for $PM_{2.5}$ 2004–2009	PM_{10}: 3 $PM_{2.5}$: 4
Marseille	Cinq Avenues	PM_{10}, $PM_{2.5}$, SO_2, O_3, NO_2	43°18′22″N	5°23′43″E	Urban background	2001–2008	PM_{10}: 2 $PM_{2.5}$: 24 NO_2: 1 O_3: 8 SO_2: 25
Marseille	Timone	PM_{10}, SO_2, NO_2, CO	43°17′24″N	5°24′86″E	Traffic	2001–2008	PM_{10}, NO_2, CO: 2 SO_2: 25
Milan	Verziere	PM_{10}, CO, NO_2, O_3	45°27′46″N	9°11′45E	Traffic	2006–2010	≤1
Milan	Pascal Città Studi	PM_{10}, $PM_{2.5}$, CO, NO_2, O_3	45°28′43″N	9°14′4″E	Urban background	2006–2010	PM_{10}, NO_2: 0 $PM_{2.5}$: 10 O_3: 1 CO: 25
Modena	Parco Ferrari	PM_{10}, $PM_{2.5}$, NO_2, O_3	44°39′5N	10°54′26E	Urban background	2008–2010	PM_{10}, NO_2, O_3: ≤1 $PM_{2.5}$: 10
Modena	Giardini	CO, NO_2	44°38′13N	10°54′21E	Traffic	2008–2010	CO: 3 NO_2: <1
Parma	Montebello	PM_{10}, NO_2	44°47′24N	10°20′24E	Traffic	2008–2010	2
Parma	Cittadella	PM_{10}, $PM_{2.5}$, CO, NO_2, O_3	44°47′60N	10°19′48E	Urban background	2008–2010	PM_{10}, $PM_{2.5}$: 2 NO_2: 0 CO, O_3: 6
Reggio-Emilia	San Lazzaro	PM_{10}, $PM_{2.5}$, NO_2, O_3	44°21′20N	10°41′49E	Urban background	2008–2010	PM_{10}: 2 $PM_{2.5}$: 5 NO_2: <1 O_3: 9
Reggio-Emilia	Timavo	PM_{10}	44°41′52N	10°37′28E	Traffic	2008–2010	PM_{10}: <1
Rome	Villa Ada	PM_{10}, $PM_{2.5}$, SO_2, CO, NO_2, O_3	41°55′58N	12°30′25E	Urban background	2006–2010	PM_{10}, $PM_{2.5}$, CO, NO_2, O_3: <1 SO2: 20
Rome	Arenula	PM_{10}, $PM_{2.5}$	41°53′38N	12°28′31E	Traffic	2006–2010	<1
Rome	Magna Grecia	CO, NO_2	41°52′59N	12°30′32E	Traffic	2006–2010	<1
Thessaloniki	University	SO_2, CO, O_3, NO_2	40°37′38N	22°56′34E	Urban, traffic influenced	2007–2010	NO_2: 16 SO_2, CO, O_3: 25 O_3: 11
Thessaloniki	Egnatia	PM_{10}, $PM_{2.5}$	40°38′15 N	22°56′30E	Traffic	2007–2010	PM_{10}: 0 $PM_{2.5}$: 20
Thessaloniki	Eptapyrgio	PM_{10}, $PM_{2.5}$	40°38′34N	22°57′38E	Urban background	2007–2010	0
Turin	Consolata	PM_{10}, SO_2, CO	45°04′43 N	7°40′47E	Traffic	2006–2010	PM_{10}: 8 CO: 2 SO_2: 10
Turin	Lingotto	$PM_{2.5}$	45°05′10N	7°39′32E	Urban background	2006–2010	9
Turin	Rebaudengo	SO_2, CO, NO_2	45°06′20N	7°38′6E	Traffic	2006–2010	SO_2: 10 CO: 3 NO_2: 6
Turin	Gaidano	PM_{10}, CO, NO_2	45°03′5N	7°39′2E	Urban background	2006–2010	PM_{10}: 12 NO_2: 2 CO: 4

1. Introduction

Air pollution has been the subject of intensive investigation mainly because of their impact on health (Andreson et al., 2012; Pope and Dockery, 2006), the Earth's climate (IPCC, 2007), visibility, ecosystems and building materials. To improve air quality, the European Commission has established limit values for the main ambient air pollutants through the Directive 2008/50/EC (EU, 2008), which regulates ambient air concentrations of SO_2, NO_2, NO_x, PM_{10}, $PM_{2.5}$, Pb, C_6H_6, CO and O_3 and the Directive 2004/107/EC (EU, 2004) related to As, Cd, Hg, Ni and PAH (including BaP) in ambient air.

Recently, several studies have observed decreasing trends for particulate matter, PM concentrations PM_{10} and $PM_{2.5}$ in many European sites (Tsyro et al., 2011; Barmpadimos et al., 2012; Cusack et al., 2012; Salvador et al., 2012). Nevertheless, the current policy efforts, at the EU and the national level, have not fully delivered the expected results. In spite of the significant improvements, serious air pollution impacts still persist. The existing air quality limit/target values for PM_{10}, $PM_{2.5}$, NO_2 and O_3 are currently being exceeded at several locations throughout Europe (EEA, 2012). The lowest concentrations of PM_{10}, $PM_{2.5}$ and NO_2 are generally found in Northern Europe and the highest in Southern and Eastern Europe (Putaud et al., 2004, 2010; Eeftens et al., 2012; Cyrys et al., 2012). The elevated concentrations observed in Southern Europe and Mediterranean countries in particular, are attributed to the combination of diverse emission sources affecting the Mediterranean Basin including industry, traffic, resuspended dust, shipping emissions and African dust intrusions with a climate characterized by arid conditions as well as high radiation and photochemical conversion rates that significantly enhance air pollution levels (Karanasiou et al., 2007, 2009; Rodriguez et al., 2007; Eleftheriadis et al., 2006; Querol et al., 2004; Lelieveld et al., 2002).

To design and implement appropriate policies for the mitigation of air pollution, information on air pollutant trends and variability is needed. However, for the Mediterranean Basin a thorough assessment of the long-term PM trends has not been conducted yet.

Long-term data of ambient concentrations of $PM_{2.5}$, PM_{10}, and gaseous pollutants: CO, SO_2, NO_2 and O_3 were collected from the monitoring networks in traffic and urban background sites in four Southern European countries (Spain, France, Italy and Greece) in the framework of the MED-PARTICLES project (particles size and composition in Mediterranean countries: geographical variability and short term health effects, http://www.epidemiologia.lazio.it/medparticles/index.php/en/). The objective of MED-PARTICLES is to characterize particulate pollution and its health effects across Mediterranean countries. In this paper the spatial and temporal variations and long-term trends of air pollutants are investigated in order to assess the variability observed within Southern Europe. Future work includes the characterization of PM composition and the quantification of emission sources in the Mediterranean Basin which will be further used to examine the health effects caused by specific chemical components and sources.

2. Air pollution data

$PM_{2.5}$ and PM_{10}, gaseous pollutant (CO, SO_2, NO_2 and O_3) data as well as meteorological parameters: mean daily temperature, relative humidity, wind speed and direction were provided by the monitoring networks established in each city participating in the MED-PARTICLES project. All particle measurements were obtained using the gravimetric method or an equivalent one (beta-attenuation), except measurements in Marseille that were provided from the tapered element oscillating microbalance (TEOM) method. It should be mentioned that the TEOM and beta-attenuation methods tend to underestimate the PM_{10} concentrations when compared to the gravimetric ones, with seasonal variations, i.e. a good comparison is established during summer, and an underestimation of 10–30% is found during winter (Hauck et al., 2004). To obtain PM_{10} concentrations, the EC Guidance

Table 2
Average concentrations (mean, 25th percentile, 75th percentile) for NO_2, SO_2, O_3 and CO.

City	NO_2			SO_2			O_3			CO		
Traffic sites, µg m^{-3}	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile
Athens	53.2	40.0	64.2	6.4	3.0	8.2	78.0	52.0	84.0	2.7	1.8	3.5
Barcelona	67.9	50.0	82.0	4.5	2.4	6.2	36.6	20.7	51.4	0.6	0.3	0.8
Bologna	57.7	45.0	69.8	–	–	–	–	–	–	1.0	0.7	1.2
Huelva	–	–	–	–	–	–	–	–	–	–	–	–
Madrid	58.5	41.1	73.2	14.8	9.0	18.6	40.2	22.2	56.4	0.7	0.3	0.9
Marseille	52.0	39.0	65.0	12.9	5.3	18.7	–	–	–	0.7	0.3	1.0
Milan	64.0	46.0	79.0	–	–	–	56.0	18.9	84.0	1.4	0.8	1.8
Modena	54.7	43.3	65.2	–	–	–	–	–	–	0.9	0.6	1.2
Parma	44.3	30.9	56.3	–	–	–	–	–	–	–	–	–
Reggio Emilia	43.6	32.5	52.6	–	–	–	–	–	–	–	–	–
Rome	71.1	57.7	83.8	–	–	–	–	–	–	1.3	1.0	1.5
Thessaloniki	55.2	45.0	64.2	4.3	2.1	4.3	41.9	25.0	52.0	1.4	1.0	1.8
Turin	75.2	57.8	90.8	–	–	–	–	–	–	1.09	0.55	1.54
Urban background sites, µg m^{-3}	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile	Mean	25th percentile	75th percentile
Athens	21.6	14.3	28.0	8.1	3.0	11.1	87.1	60.6	111	1.0	0.5	1.2
Barcelona	39.7	27.5	50.3	2.9	1.0	4.0	39.7	22.8	55.0	0.4	0.3	0.5
Bologna	42.8	28.3	56.5	–	–	–	63.2	28.8	92.5	–	–	–
Huelva	14.3	7.5	19.4	6.7	3.5	8.5	62.9	48.9	77.0	0.8	0.7	0.9
Madrid	40.2	28.4	56.0	9.3	6.0	13.5	48.7	36.3	69.0	0.5	0.2	0.7
Marseille	35.1	23.8	45.0	4.8	1.2	7.4	51.7	32.5	69.6	–	–	–
Milan	55.0	36.0	70.0	–	–	–	64.3	19.7	102	–	–	–
Modena	–	–	–	–	–	–	–	–	–	–	–	–
Parma	31.4	18.7	42.9	–	–	–	68.5	28.8	103	–	–	–
Reggio Emilia	34.9	23.2	45.6	–	–	–	70.5	29.4	106	–	–	–
Rome	39.4	28.2	49.3	1.1	0.5	1.6	67.4	39.5	94.0	0.7	0.5	0.9
Thessaloniki	42.1	30.5	53.6	9.9	4.4	13.4	56.0	28.4	84.5	0.6	0.4	0.8
Turin	47.9	30.5	62.0	5.5	3.2	7.0	68.6	23.9	105	0.8	0.1	1.2

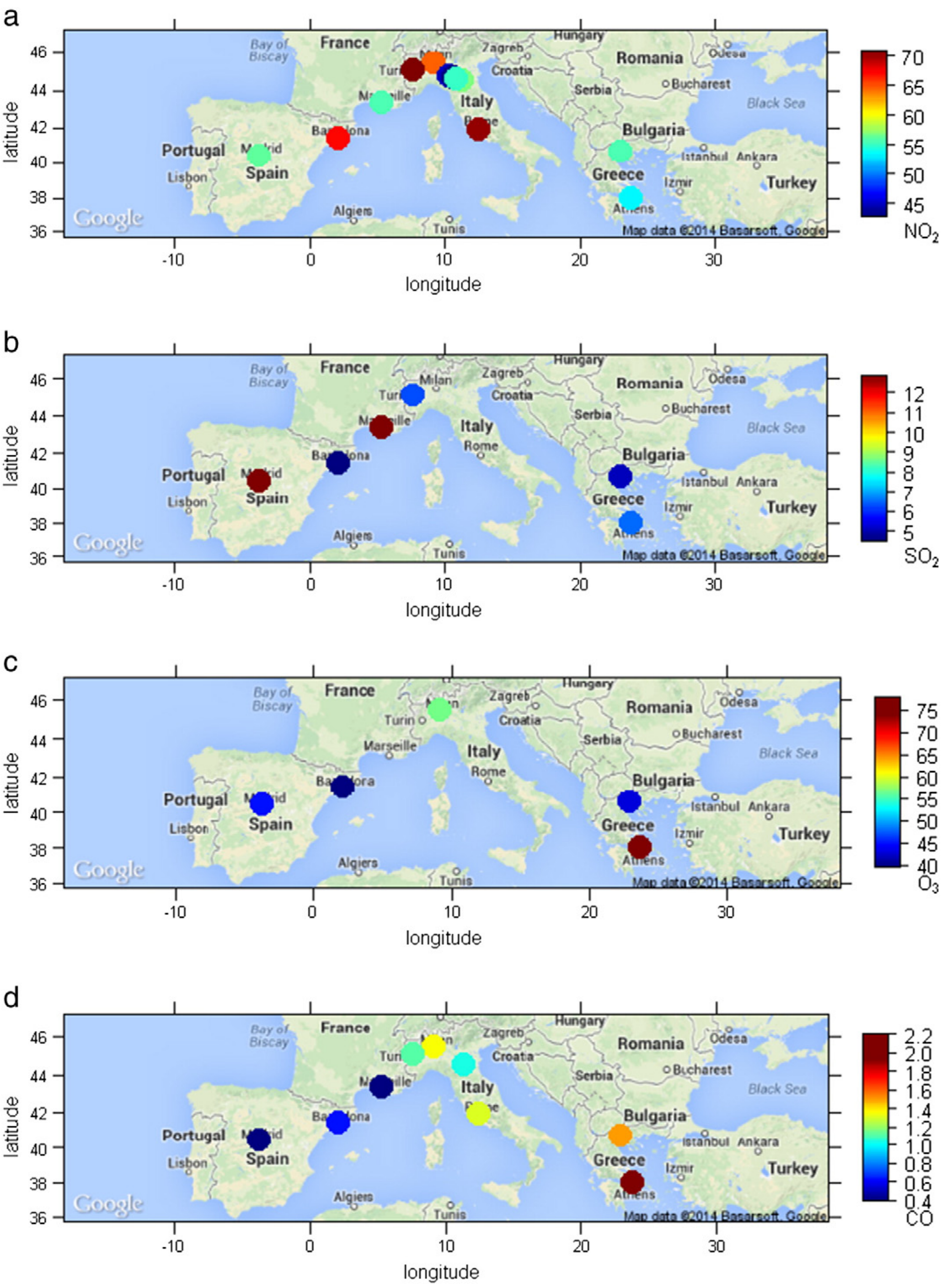

Fig. 1. Average concentrations of a) NO_2, b) SO_2, c) O_3 and d) CO in traffic sites in Southern Europe.

Document Williams and Bruckmann, 2001 states that Member States should compare the method they use with the EN12341 reference method (gravimetric method) and correct the measurements by a relevant factor to produce results equivalent to those that would have been achieved by using the reference method.

The data collection protocol followed the one applied in the APHEA project (Katsouyanni et al., 1997). The sampling period that we studied is 2001–2010. The monitoring sites selected are both traffic and urban background sites that covered at least 3 consecutive years in the period 2001–2010 comprising annual data coverage larger than 75% and also depending on the availability of $PM_{2.5}$ measurements. Most of the analyses have been carried out with the OpenAir software package (Carslaw and Ropkins, 2012) using the R language (R Development Core Team, 2011). Table 1 provides the characteristics of the selected sites for the sampling period 2001–2010.

3. Results and discussion

3.1. Average concentration values of gaseous pollutants

3.1.1. Intra-area variation of gaseous pollutants

The long-term average concentrations of gaseous pollutants and the 25th and 75th percentiles for the traffic and urban background sites in the different cities across Southern Europe are presented in Table 2

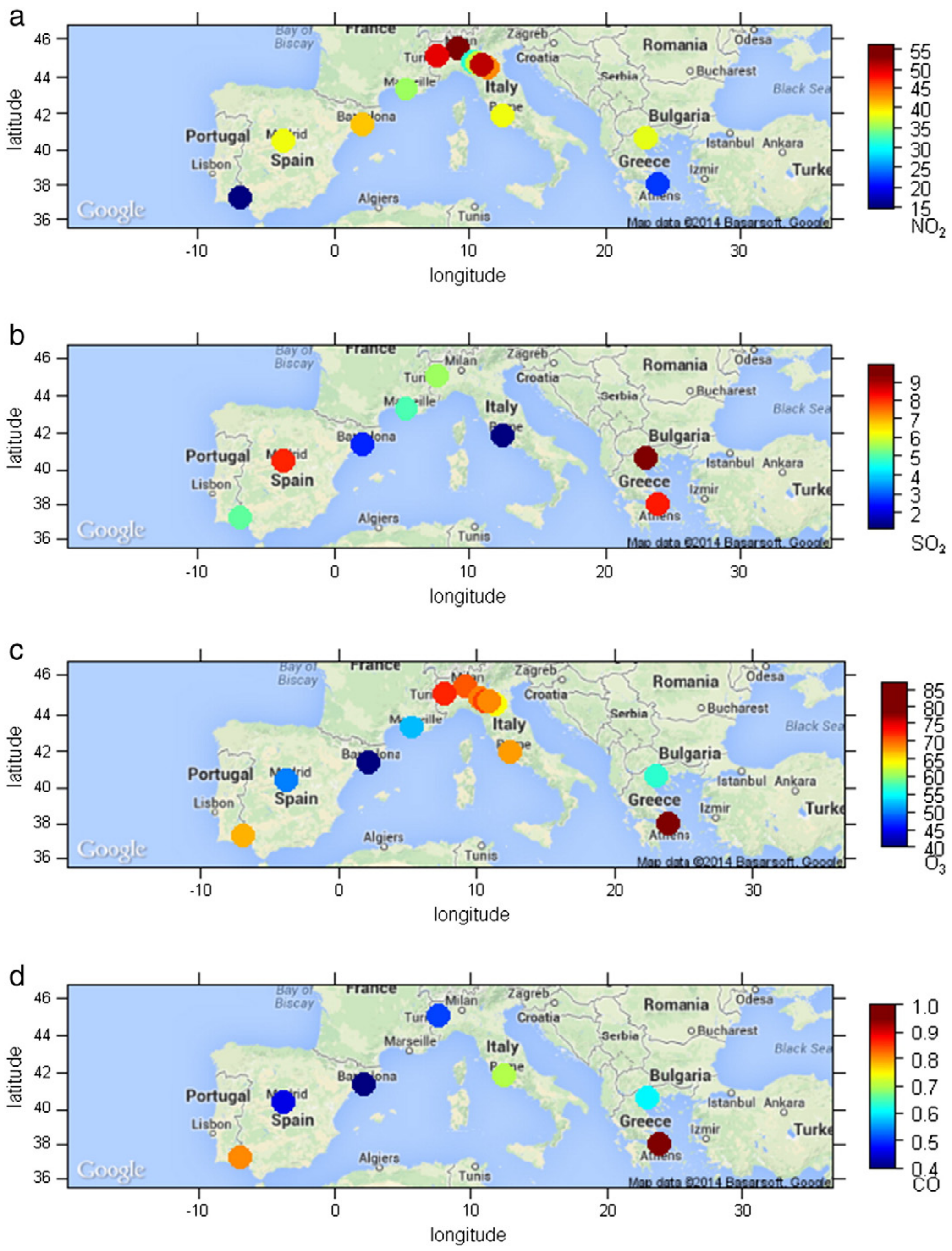

Fig. 2. Average concentrations of a) NO_2, b) SO_2, c) O_3 and d) CO in urban background sites in Southern Europe.

(the whole sampling period was taken into account to examine the intra-area variation).

As expected, a trend is observed for NO_2 with higher concentrations at the traffic stations, compared to the ones registered at the urban background sites. In the traffic sites levels of NO_2 were high, ranging from 44 to 75 μg m^{-3} exceeding the established annual limit value of 40 μg m^{-3} (Directive 2008/50/EC) indicating the strong influence of road traffic emissions on air quality. Generally, the NO_2 levels in Southern Europe are higher that those observed in northern countries (Cyrys et al., 2012). This fact was attributed to the higher traffic density, and to the higher conversion of NO to NO_2 because of relatively high temperatures and ozone concentrations.

For SO_2 concentrations, the intra-city trend is not clear. In Athens and Thessaloniki the mean SO_2 levels were higher in the urban background sites (e.g.: in Athens the mean SO_2 concentration was 6.4 μg m^{-3} at the traffic site and 8.1 μg m^{-3} at the urban background site). The opposite trend was observed in Barcelona, Madrid and Marseille where the higher concentrations were registered at the traffic sites.

Higher O_3 concentrations were measured in the urban background sites (40–87 μg m^{-3}) than in the traffic sites (37–78 μg m^{-3}) since in traffic and urban areas with elevated fresh emissions of NO, some of the O_3 present is depleted while oxidizing NO to NO_2.

A clear trend was observed for CO with higher values in the traffic sites due to its direct association with the emissions from the incomplete combustion of fossil fuels and biofuels.

Table 3
Average concentrations (mean, standard deviation, minimum, maximum) for PM_{10} and $PM_{2.5}$.

City	PM_{10}				$PM_{2.5}$			
Traffic sites, µg m^{-3}	Mean	SD	Min	Max	Mean	SD	Min	Max
Athens	50.6	19.1	14	123	30.11	11.61	9.0	70.0
Barcelona	42.6	17.7	6.0	81.0	24.6	15.2	2.5	48.4
Bologna	37.1	18.7	4.0	103	24.2	14.8	2.5	81.0
Huelva	–	–	–	–	–	–	–	–
Madrid	34.4	17.2	5.1	93.5	16.7	8.5	1.1	46.2
Marseille	32.5	11.1	7.1	67.6	–	–	–	–
Milan	45.3	29.0	1.6	188	–	–	–	–
Modena	39.5	21.2	3.0	109	–	–	–	–
Parma	33.9	17.4	2.0	94	–	–	–	–
Reggio-Emilia	40.6	20.3	5.0	110	–	–	–	–
Rome	36.7	14.4	1.8	83.0	19.7	8.8	1.5	49.4
Thessaloniki	53.5	24.8	13.7	211	38.6	13.7	1.0	110
Turin	51.9	32.8	4.1	158	–	–	–	–
Urban background sites, µg m^{-3}	Mean	SD	Min	Max	Mean	SD	Min	Max
Athens	27.4	15.8	6.0	158	18.2	7.2	4.0	44.0
Barcelona	34.7	15.3	1.0	88.0	23.0	10.2	1.2	58.4
Bologna	–	–	–	–	–	–	–	–
Huelva	39.4	17.3	7.9	102	19.3	9.3	1.0	50.1
Madrid	26.2	13.9	3.7	72.7	12.1	5.7	2.1	31.0
Marseille	26.0	9.7	4.3	57.2	17.2	7.8	2.6	43.3
Milan	46.3	32.6	1.0	190	32.8	27.1	1.0	177
Modena	37.0	20.0	1.0	104	37.0	20.0	12.5	1.0
Parma	31.1	15.9	1.0	86.7	19.9	13.4	1.0	68.0
Reggio-Emilia	31.0	16.5	2.0	89	20.6	12.7	1.0	64.0
Rome	28.3	13.2	1.0	105	18.4	9.7	1.0	51.0
Thessaloniki	32.5	17.6	2.6	202	19.9	9.8	1.6	98.3
Turin	46.3	33.0	1.0	157	32.9	25.5	4.0	118

3.1.2. Inter-area variation of gaseous pollutants

As the availability of data was different for each city, in order to investigate the inter-area variation we used the period 2007–2009 in which data were available for all cities. For the sites of Modena, Parma and Reggio-Emilia for which data were not available for 2007 the selected period was 2008–2009. Figs. 1 and 2 provide the average concentrations of gaseous pollutants at the traffic and urban background sites for the selected period.

In general the variation of the measured concentrations did not vary significantly between the different cities. The highest mean concentrations of NO_2 for the period 2007–2009 were found in Turin, Rome, Barcelona and Milan traffic sites at 71 µg m^{-3}, 70 µg m^{-3}, 67 µg m^{-3} and 65 µg m^{-3} respectively. In these sites the large fraction of diesel-powered vehicles is thought to be the main responsible factor for the high NO_2 emission rates (Fig. 1a). Comparing the urban background sites the Italian cities Milan, Modena, Turin, and Bologna showed the highest NO_2 values of 56 µg m^{-3}, 51 µg m^{-3}, 49 µg m^{-3} and 43 µg m^{-3} respectively (Fig. 2a).

Concerning SO_2 concentrations between the studied cities, similar concentration levels were observed for Athens, Thessaloniki, Barcelona and Turin traffic sites, in the range 4.5–6.4 µg m^{-3} (Fig. 1b). The maximum mean values were recorded in Marseille and Madrid with average concentrations of 12.6, and 12.3 µg m^{-3} respectively. SO_2 in the urban area of Madrid reflected the influence of domestic heating as fuel oil boilers and a small percentage of coal boilers were in use during the studied period (Salvador et al., 2012; Artiñano et al., 2003). In Marseille the petrochemical activities, industrial emissions and shipping are believed to cause elevated levels of SO_2. For the urban background sites (Fig. 2b) important SO_2 concentrations were registered in Athens, Thessaloniki and Madrid attributed mainly to domestic heating emissions as in Athens and Thessaloniki fuel oil boilers are the predominant heating system (Kassomenos

Table 4
Average $PM_{2.5}/PM_{10}$ ratios and standard variation in the studied cities.

City	Site	Station type	$PM_{2.5}/PM_{10}$	R^2 $PM_{2.5}$, PM_{10}	R^2 $PM_{2.5}$, $PM_{2.5-10}$	Sampling period
Athens	Agia Paraskevi	Urban background	0.67 ± 0.14	0.68	0.35	2007–2009
Athens	Peiraias	Traffic	0.60 ± 0.20	0.60	−0.13	2007–2009
Barcelona	Palau Reial	Urban background–traffic influenced	0.67 ± 0.16	0.80	0.07	2003–2010
Barcelona	Sant Gervasi	Traffic	0.58 ± 0.22	0.84	0.10	2004–2010
Bologna	San Felice	Traffic	0.64 ± 0.14	0.92	0.16	2006–2010
Huelva	Campus	Urban background–influenced by industry	0.38 ± 0.11	0.60	−0.03	2003–2010
Madrid	Cuatro Caminos	Urban–traffic	0.51 ± 0.13	0.89	0.48	2004–2009
Madrid	Casa de Campo	Urban background	0.50 ± 0.15	0.88	0.60	2004–2009
Marseille	Cinq Avenues	Urban background	0.65 ± 0.14	0.86	0.13	2001–2008
Milan	Pascal Città Studi	Urban background	0.65 ± 0.18	0.95	0.54	2006–2010
Modena	Parco Ferrari	Urban background	0.56 ± 0.13	0.94	0.61	2008–2010
Parma	Citadella	Urban background	0.61 ± 0.18	0.89	0.09	2006–2010
Reggio-Emilia	San Lazzaro	Urban background	0.65 ± 0.12	0.96	0.59	2006–2010
Rome	Villa Ada	Urban background	0.65 ± 0.16	0.88	0.12	2006–2010
Rome	Arenula	Traffic	0.54 ± 0.13	0.84	0.34	2006–2010
Thessaloniki	Egnatia	Traffic	0.64 ± 0.10	0.90	0.60	2007–2009
Thessaloniki	Eptapyrgio	Urban background	0.61 ± 0.12	0.91	0.61	2007–2009

et al., 2011). However, the observed values were significantly lower than the established limit value (125 μg m^{-3}) as a result of the adopted measures to reduce the sulfur content in fuels, coupled with the shift towards the use of cleaner fuels and the improvement of the efficiency of engines (Henschel et al., 2013).

The highest O_3 levels were recorded in Athens (annual average reached 87 μg m^{-3} at the urban background site and 78 μg m^{-3} at the traffic site) as a consequence of the hot and dry summers that lead to elevated O_3 concentrations.

The highest CO levels were measured in Athens (Figs. 1d and 2d). However, the recorded CO values in all cities were well below the established limit value of 10 mg m^{-3}.

3.2. Average PM concentration levels

3.2.1. Intra-area variation of PM

Table 3 gives the average concentrations, standard deviation, and minimum and maximum values of PM_{10} and $PM_{2.5}$ for the whole sampling period in order to examine the intra-city differences and similarities. PM_{10} and $PM_{2.5}$ concentrations were higher at the traffic sites than those at the urban background sites for all studied areas. PM_{10} mean values were found in the range of 42–52 μg m^{-3} at the traffic sites while those at the urban background sites varied from 26 to 46 μg m^{-3}. $PM_{2.5}$ mean levels ranged from 17 to 37 μg m^{-3} at the traffic sites and from 12 to 37 μg m^{-3} at the urban background sites. The ratio PM_{10}urban background/PM_{10}traffic was in the range of 0.55–0.98 and the ratio $PM_{2.5}$urban background/$PM_{2.5}$traffic was within the range of 0.52–0.95.

$PM_{2.5}$ and PM_{10} concentrations have the same pattern as the correlation between these two size fraction is high ($R^2 > 0.60$) in all monitoring sites (Table 4). On the other hand, the correlation of $PM_{2.5}$ with the coarse fraction $PM_{2.5-10}$ was lower revealing the different sources and processes affecting these two size fractions. $PM_{2.5}/PM_{10}$ ratios across Southern Europe were generally within the range of 0.50–0.67 with the only exception of Huelva (mean ratio of 0.38) indicating that fine particles comprise a large fraction of PM_{10} (Table 4). The $PM_{2.5}/PM_{10}$ ratios were slightly higher in the urban background sites than those in the traffic ones e.g. Rome and Athens. It seems that although in traffic sites the concentrations of both $PM_{2.5}$ and PM_{10} were significantly higher than those measured in urban background sites, the coarse fraction $PM_{2.5-10}$ was higher at the traffic sites. This fact is due to the high levels of resuspended dust in sites highly affected by road traffic. Previous studies have demonstrated that road dust is one of the major sources in urban agglomerations with its mass contribution being more important in Southern European cities (Karanasiou et al., 2009, 2011; Amato et al., 2011). On the other hand in sites less contaminated like urban background sites the secondary aerosol sources, which produce fine particles, are predominant (Van Dingenen et al., 2004).

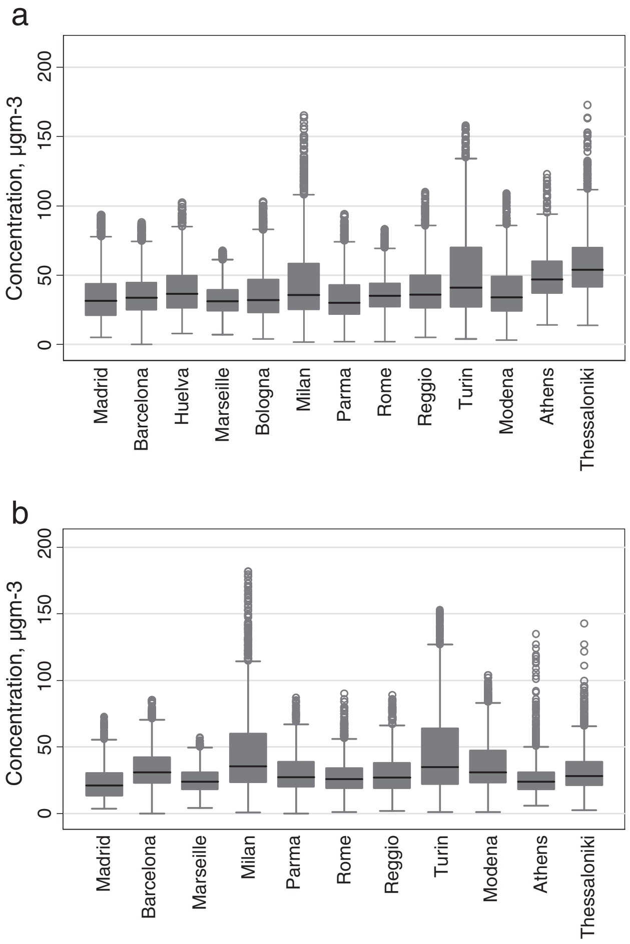

Fig. 3. Distribution of PM_{10} daily concentrations (μg m^{-3}) in a) traffic and b) urban background sites across Southern Europe. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown as points.

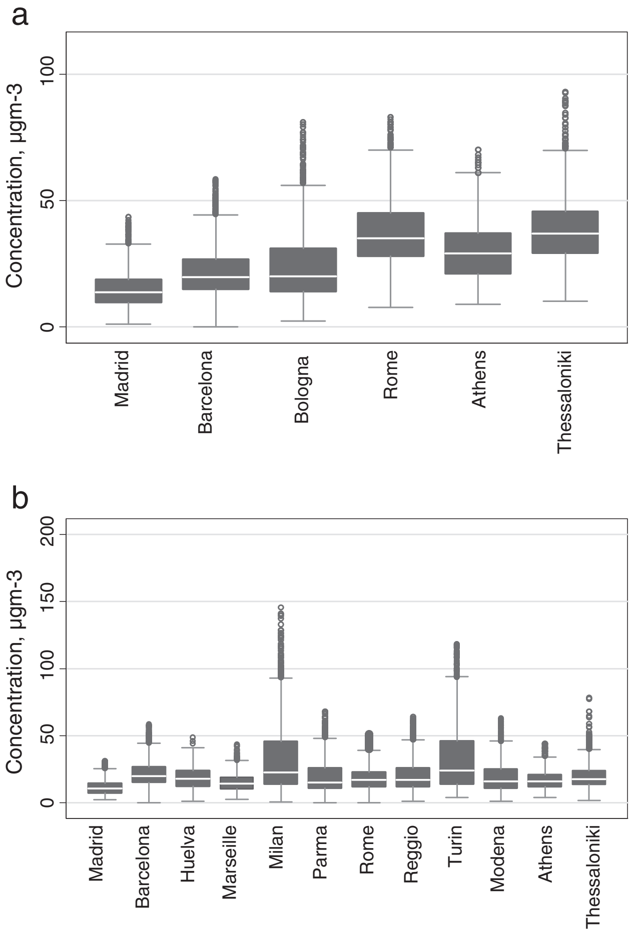

Fig. 4. Distribution of $PM_{2.5}$ daily concentrations (μg m^{-3}) in a) traffic and b) urban background sites across Southern Europe. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown as points.

Table 5
Pearson correlation coefficients, R^2 between PM_{10}, ($PM_{2.5}$) and NO_2, SO_2, O_3 and CO.

City	NO_2	SO_2	O_3	CO
Traffic sites				
Athens	0.40	0.18	−0.21	0.56
	(0.46)	0.21	−0.22	0.28
Barcelona	0.65	0.35	−0.28	0.44
	(0.66)	(0.36)	(−0.25)	(0.42)
Bologna	0.57	–	–	0.57
	(0.55)			(0.54)
Huelva	–	–	–	–
Madrid	0.64	0.40	−0.30	0.48
	(0.61)	(0.30)	(−0.31)	(0.46)
Marseille	0.58	0.40	–	0.44
	(−)	(−)	(−)	(−)
Milan	0.75		−0.49	0.60
Modena	0.63			0.30
Parma	0.65	–	–	–
	(−)	(−)	(−)	(−)
Reggio Emilia	–	–	–	–
	(−)	(−)	(−)	(−)
Rome	0.51	–	–	0.54
	(0.52)	–	–	(0.50)
Thessaloniki	–	–	–	–
	(−)	(−)	(−)	(−)
Turin	0.61	0.58	–	0.65
	(−)	(−)	(−)	(−)
Urban background sites				
Athens	0.36	0.13	0.18	0.11
	(0.30)	(0.17)	(0.28)	(0.10)
Barcelona	0.35	0.21	−0.21	0.20
	(0.36)	(0.18)	(−0.26)	(0.22)
Bologna	–	–	–	–
Huelva	0.49	0.39	0.05	0.28
	(0.47)	(0.40)	(0.02)	(0.36)
Madrid	0.46	0.48	−0.30	0.49
	(0.48)	(0.45)	(−0.33)	(0.50)
Marseille	0.53	0.25	−0.10	–
	(0.73)	(0.26)	(−0.40)	–
Milan	0.69	–	−0.52	0.40
	(0.67)	(−)	(−0.58)	(0.39)
Modena	0.62	–	−0.26	–
	(0.60)	(−)	(−0.28)	(−)
Parma	0.56	–	−0.36	0.54
	(0.66)	(−)	(−0.48)	(0.61)
Reggio Emilia	0.63	–	−0.40	–
	(0.66)	(−)	(−0.48)	(−)
Rome	0.50	0.34	−0.22	0.48
	(0.56)	(0.30)	(−0.30)	(0.60)
Thessaloniki	0.60	0.15	0.38	0.54
	(0.68)	(0.12)	(0.39)	(0.50)
Turin	0.66	0.62	−0.55	0.64
	(0.72)	(0.61)	(−0.60)	(0.66)

3.2.2. Inter-area variation of PM

For comparison reasons as for the gaseous pollutants we selected the period 2007–2009 for which data were available for all sites with the exception of the sites of Modena, Parma and Reggio-Emilia. Figs. 3 and 4 show the distribution of PM_{10} and $PM_{2.5}$ daily concentrations at traffic and urban sites across Southern Europe. The average concentrations for PM across Southern Europe laid within the range of annual means typical of European sites and according to the monitoring site characteristics (traffic and urban background sites) (Querol et al., 2004; Putaud et al., 2010). A regional pattern could be observed with higher PM_{10} and $PM_{2.5}$ concentrations at the Italian and Greek cities and lower levels in Western South Europe (Barcelona, Marseille, Madrid, Huelva). However, it should be mentioned that several of the PM_{10} maximum concentrations observed in Italy and Greece usually coincided with African dust episodes that are more frequent and more intense in the central and eastern than those in the western Mediterranean Basin (Pey et al., 2013).

Regarding PM_{10} levels at the traffic sites a quite similar variation was registered in Spain (Madrid, Barcelona, Huelva), France (Marseille) and Italy (Bologna, Parma, Rome, Reggio, Modena) (Fig. 3a). The highest mean PM_{10} concentrations were observed in Athens and Thessaloniki, equal to 58 μg m^{-3} and 48 μg m^{-3}, respectively followed by PM_{10} concentrations in Turin, 42 μg m^{-3} (Fig. 3a). In Turin as in the other cities of the Po valley (Bologna, Milan, Parma, Modena and Reggio Emilia), the combination of stagnant air conditions with high emissions and high population density is the main cause of very strong pollution episodes (Cyrys et al., 2012). Similarly, the air pollution problems in Athens and Thessaloniki are the result of the high population density and the accumulation of air pollutants over the city, due to topography (basin surrounded by mountains), narrow and deep street canyons and adverse meteorological conditions (Kassomenos et al., 2011; Karanasiou et al., 2009). Thermal inversions, followed by accumulation of air pollutants in the lower layers of the atmosphere are also very common for Athens' greater area. In the urban background sites the highest

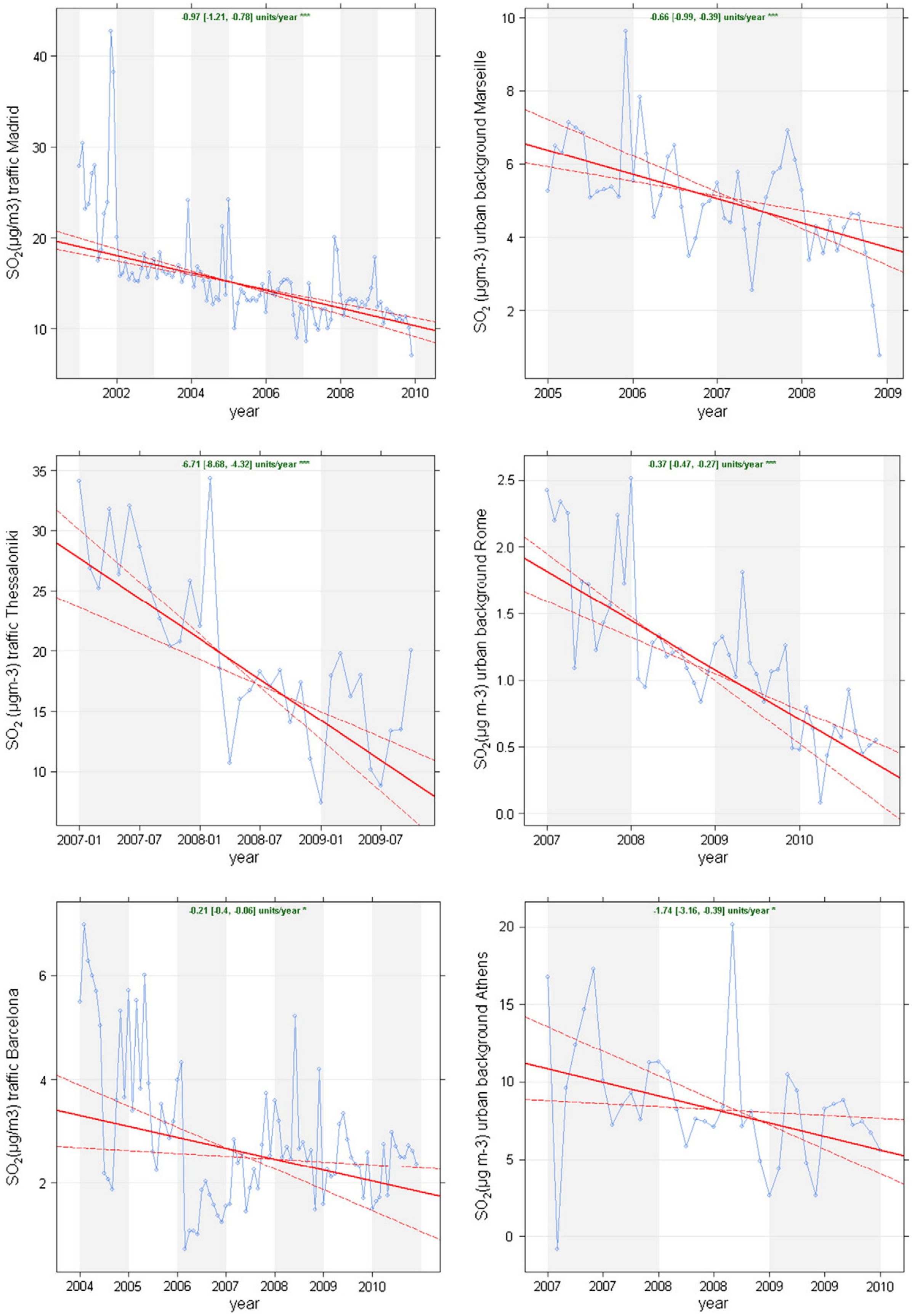

Fig. 5. Trend analysis of SO_2, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as $\mu g\ m^{-3}$ per year and the 95% confidence intervals in the slope. The type of site is given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

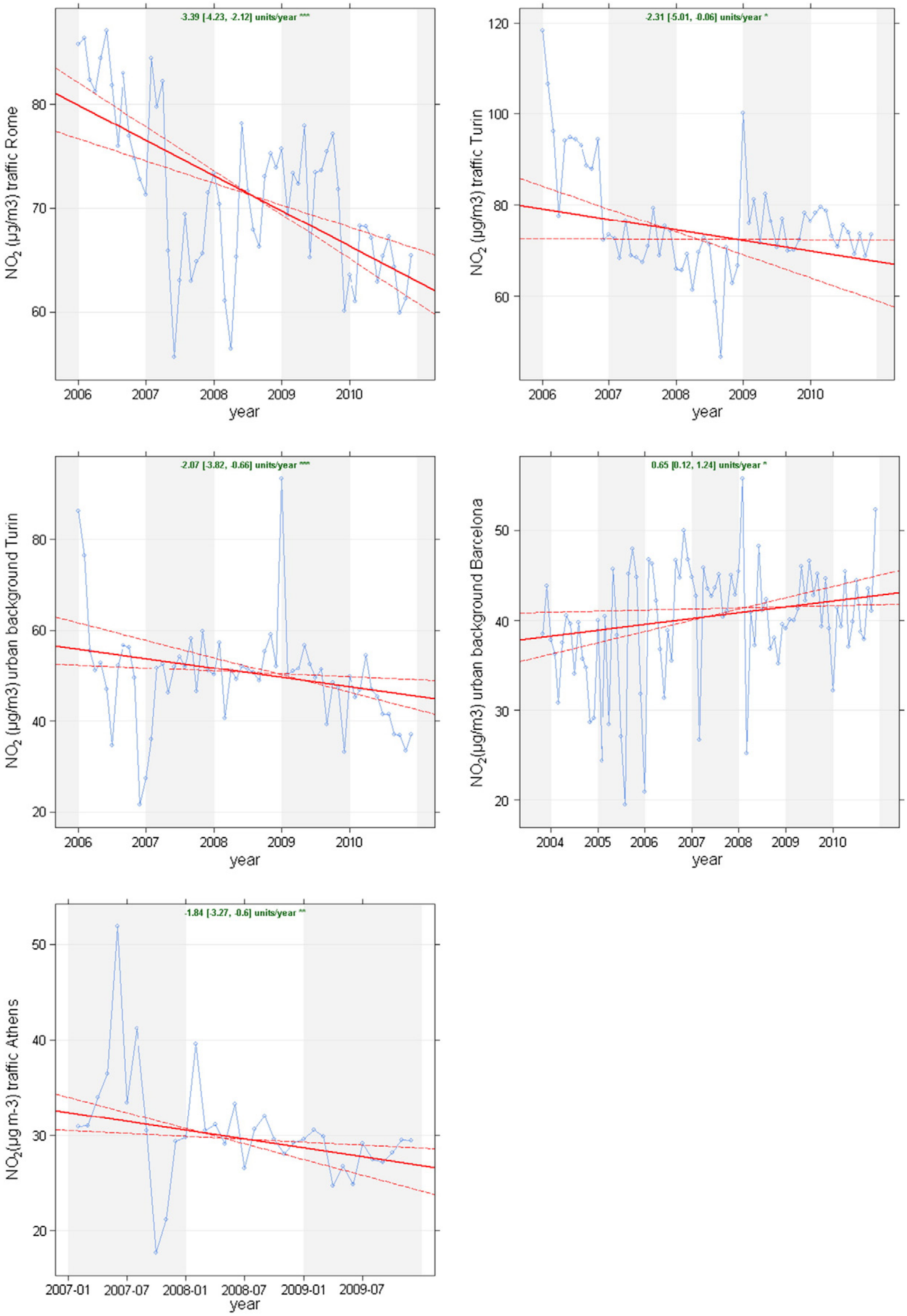

Fig. 6. Trend analysis of NO_2, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as $\mu g\ m^{-3}$ per year and the 95% confidence intervals in the slope. The type of site is given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

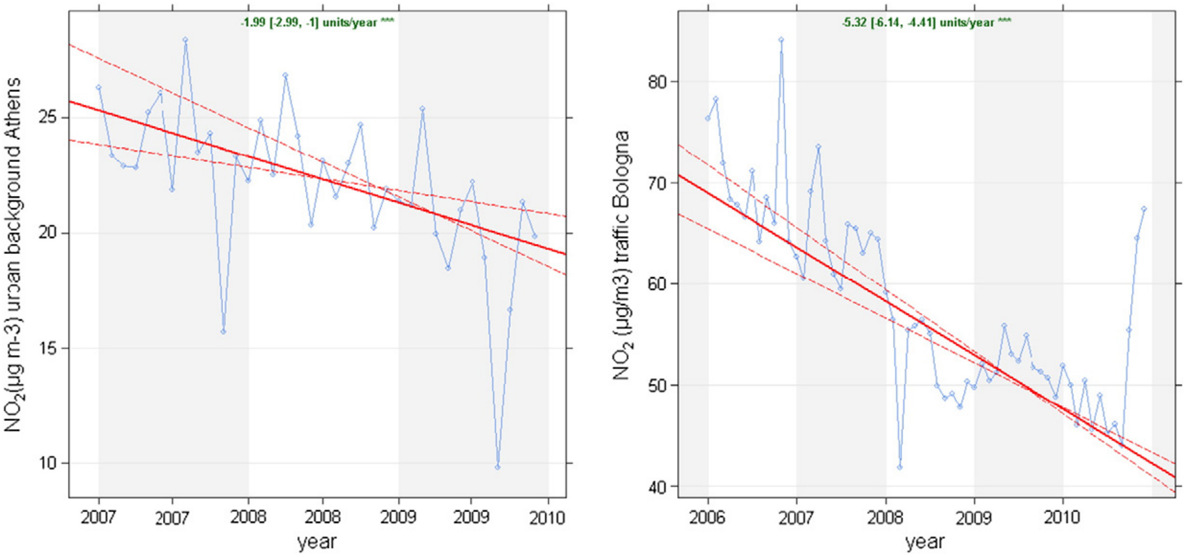

Fig. 6 (*continued*).

mean PM_{10} concentrations were recorded in Turin and Milan, 48 and 46 µg m^{-3} respectively (Fig. 3b).

A similar pattern was observed for $PM_{2.5}$ at traffic sites with the maximum mean values measured in Thessaloniki and Rome equal to 39 and 37 µg m^{-3} respectively, followed by those registered in Athens, 29 µg m^{-3} (Fig. 4a). The reason for the high annual mean concentration in Thessaloniki could be the high traffic volume in combination with the influence of industry that is located in the proximity of the urban area. In the urban background sites the $PM_{2.5}$ mass concentrations showed a small variation between the different cities with the highest mean values registered in Turin and Milan, 33 µg m^{-3} (Fig. 4b).

3.3. Correlations between air pollutants

The Pearson correlation coefficients, R^2 were calculated between particles, PM_{10} and $PM_{2.5}$ and the gaseous pollutants NO_2, SO_2, O_3 and CO at the monitoring sites (Table 5). Both PM_{10} and $PM_{2.5}$ were highly correlated with NO_2 at all sites; R^2 was in the range 0.35–0.73 reflecting their common origin, the road traffic emissions. In general, the correlation coefficients were higher at the traffic sites than those in the urban background sites especially for PM_{10} due to the stronger influence of vehicle emissions. On the other hand the correlation between particles and SO_2 was weaker with the exception of the monitoring sites in Turin ($R^2 = 0.58$–0.62, traffic and urban background sites), Madrid ($R^2 = 0.30$–0.48, traffic and urban background sites), Huelva ($R^2 = 0.39$–0.40, urban background site) and Marseille ($R^2 = 0.40$ at the traffic site). This fact was attributed to the oil combustion in industrial facilities (Turin, Huelva and Marseille) and also to domestic heating (Madrid). Not surprisingly PM_{10} and $PM_{2.5}$ were anti-correlated with O_3 ($R^2 < -0.5$) as a consequence of O_3 depletion during the oxidation of NO to NO_2. However, at the urban background sites of Athens and Thessaloniki positive weak correlations were observed indicating the formation of secondary particles and O_3 by photochemical reactions during favorable weather conditions. Finally, significant correlations were found between PM and CO ($R^2 = 0.4$–0.7) being related to primary emissions from combustion processes.

3.4. Long-term trends of air pollutants

The long term trends of the gaseous pollutants were studied using the OpenAir program (Carslaw and Ropkins, 2012). The plots in Figs. 5–10 show the deseasonalized monthly mean concentrations of NO_2, SO_2, CO, O_3, PM_{10}, and $PM_{2.5}$ (data were deseasoned by the OpenAir software, stl function). The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. Only the statistically significant trends are presented here (additional figures are given in the Supplementary material). However, some of the data series presented do not cover long time periods, so they do not permit a reliable calculation.

3.4.1. Long-term trends of gaseous pollutants

Atmospheric SO_2 concentrations have declined in almost all time series studied and only one urban background–industrial influenced site (Huelva) showed a small increasing but statistically non-significant trend (Fig. 1 in the Supplementary material). Statistical significant declining trends for SO_2 were found in Thessaloniki, Madrid, Marseille, Rome and Barcelona with the most pronounced trend at the traffic site in Thessaloniki (-6.7 µg m^{-3} per year) followed by the trend in the urban background site in Athens (-1.7 µg m^{-3} per year). However these trends were calculated from 3-year data (Fig. 5). In the sites where longer time series were available (from 5 to 8 years of continuous data), as for Barcelona, Madrid, Marseille and Rome the average SO_2 reduction ranged from -0.1 to -0.9 µg m^{-3} per year. This declining trend was the result of the various EU legislations being implemented in the respective cities, such as the EU Council Directive 2001/80/EC on the limitation of emissions from large combustion plants and the Directive 1999/32/EC limiting sulfur content in fuels for ships (Henschel et al., 2013). Furthermore, some local actions to reduce the use of sulfur-containing fuels as the reduction of the use of coal for domestic heating in Madrid have also contributed to this declining trend.

NO_2 did not present a clear trend as in most cities the patterns were not statistically significant (Fig. 2 in the Supplementary material), while statistically significant trends displayed both decreasing and increasing patterns (Fig. 6). Decreasing trends were found in Rome (traffic site), Turin and Athens (traffic and urban background sites) while in Barcelona a small increasing trend was found for the urban background station that is also highly influenced by traffic. The reduction in Rome and Turin may be attributed to the implementation of measures like the Low Emission Zone strategy. According to a recent study by Cesaroni et al. (2012) the implementation of Low Emission Zone of 39 km^2 in 2002 in Rome leaded in 58% lower NO_2 emissions from cars within the zone. In Barcelona the increasing number of diesel cars, together with the particulate filters and oxidation catalysts employed in modern diesel engines, could be the cause for the small increase observed.

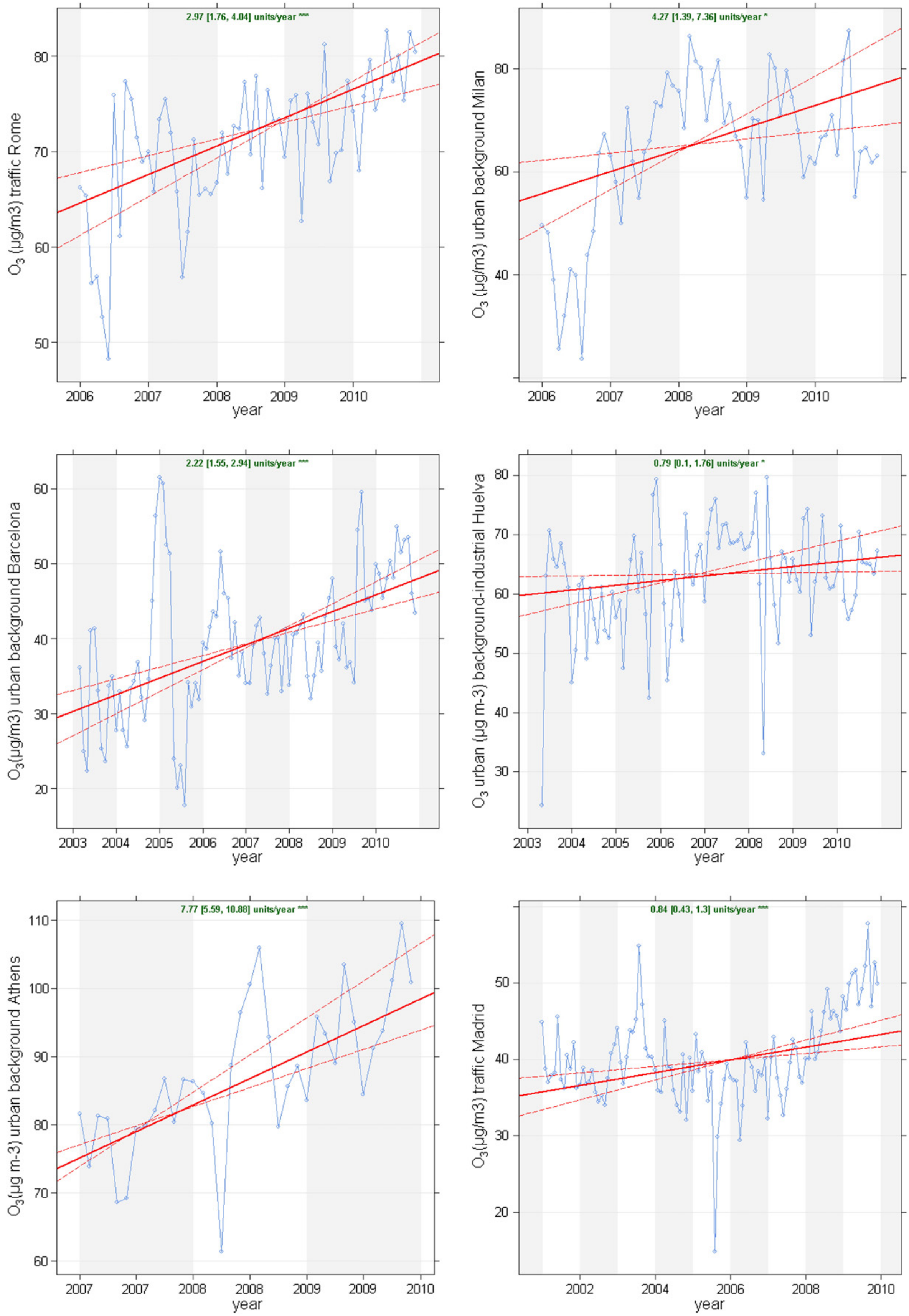

Fig. 7. Trend analysis of O_3, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as µg m^{-3} per year and the 95% confidence intervals in the slope. The type of site is given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

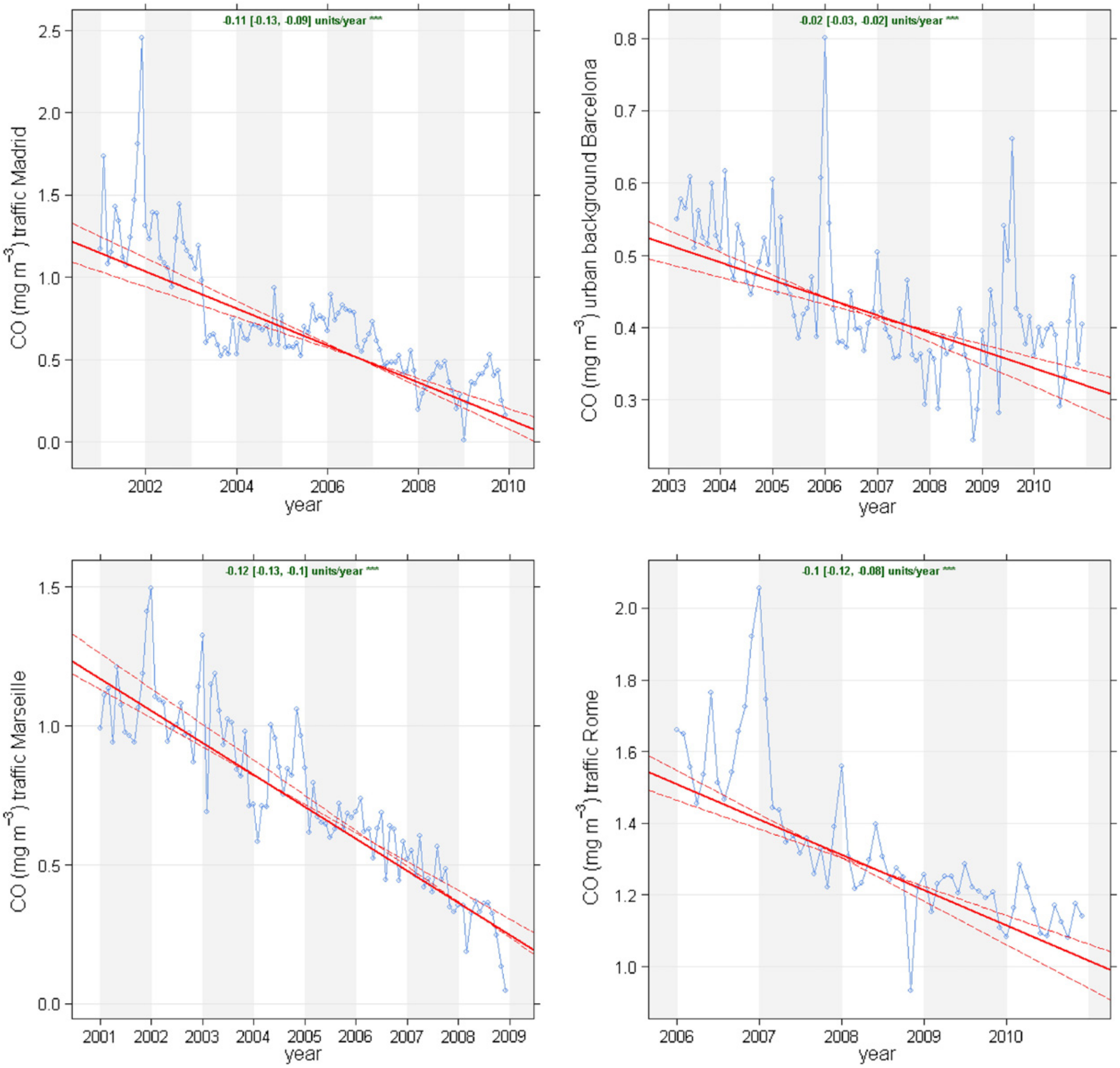

Fig. 8. Trend analysis of CO, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as μg m^{-3} per year and the 95% confidence intervals in the slope. City and type of the site are given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

The mean O_3 concentrations were markedly different from that of SO_2 (Fig. 7). In general the urban background sites revealed a rather strong increasing trend (from +0.8 to +7.8 μg m^{-3}) and only in one traffic site in Milan and Madrid the O_3 levels showed a small decrease. The decrease of NO levels may have accounted for the urban O_3 increase, although an increase of O_3 by urban O_3 production cannot be discarded.

CO atmospheric concentrations have decreased strongly during the past two decades and are generally well below the limit values (EEA, 2012). The CO concentrations in the studied sites generally had decreasing trends (Fig. 8) as a result of vehicle emission standards but also to the decrease of the percentage of gasoline cars.

3.4.2. Long-term trends of PM

The long-term trends of PM_{10} displayed a decreasing trend for most MED-PARTICLES cities despite the important variability of the concentration values (Fig. 9). For the traffic sites of Barcelona and Huelva (being the sites with the highest data coverage) the decreasing trend was ~2 μg m^{-3} per year. The Italian cities, Rome, Turin, Milan, and Bologna presented a significant decrease reaching almost 4 μg m^{-3} per year for the period 2006–2010. Also $PM_{2.5}$ concentrations revealed a decreasing tendency in the range of −0.5 to −4 μg m^{-3} per year (Fig. 10). The highest reduction was observed in Athens traffic site (−4 μg m^{-3}) followed by the decrease registered in Milan and Turin urban background sites, −2.5 and −2.1 μg m^{-3} respectively. For Barcelona urban background site and Madrid traffic site where longer data series were available a similar declining trend was observed equal to −1.5 and −1.8 μg m^{-3} per year respectively.

The decreasing trends of PM_{10} and $PM_{2.5}$ concentrations could be attributed to the effectiveness of the vehicular emission control strategies that have been implemented in Europe and the improvement in motor engine characteristics. Vehicle emissions have been regulated through a series of performance and fuel standards, including the 1998 Directive relating to the quality of petrol and diesel fuels (1998/70/EC) and vehicle emission standards, known as the Euro standards. The Euro standards cover emissions from light vehicles including passenger cars, vans, and commercial vehicles. The Euro 1 standard came into force in 1992, the Euro 2 in 1996, the Euro 3 in 2000 and the

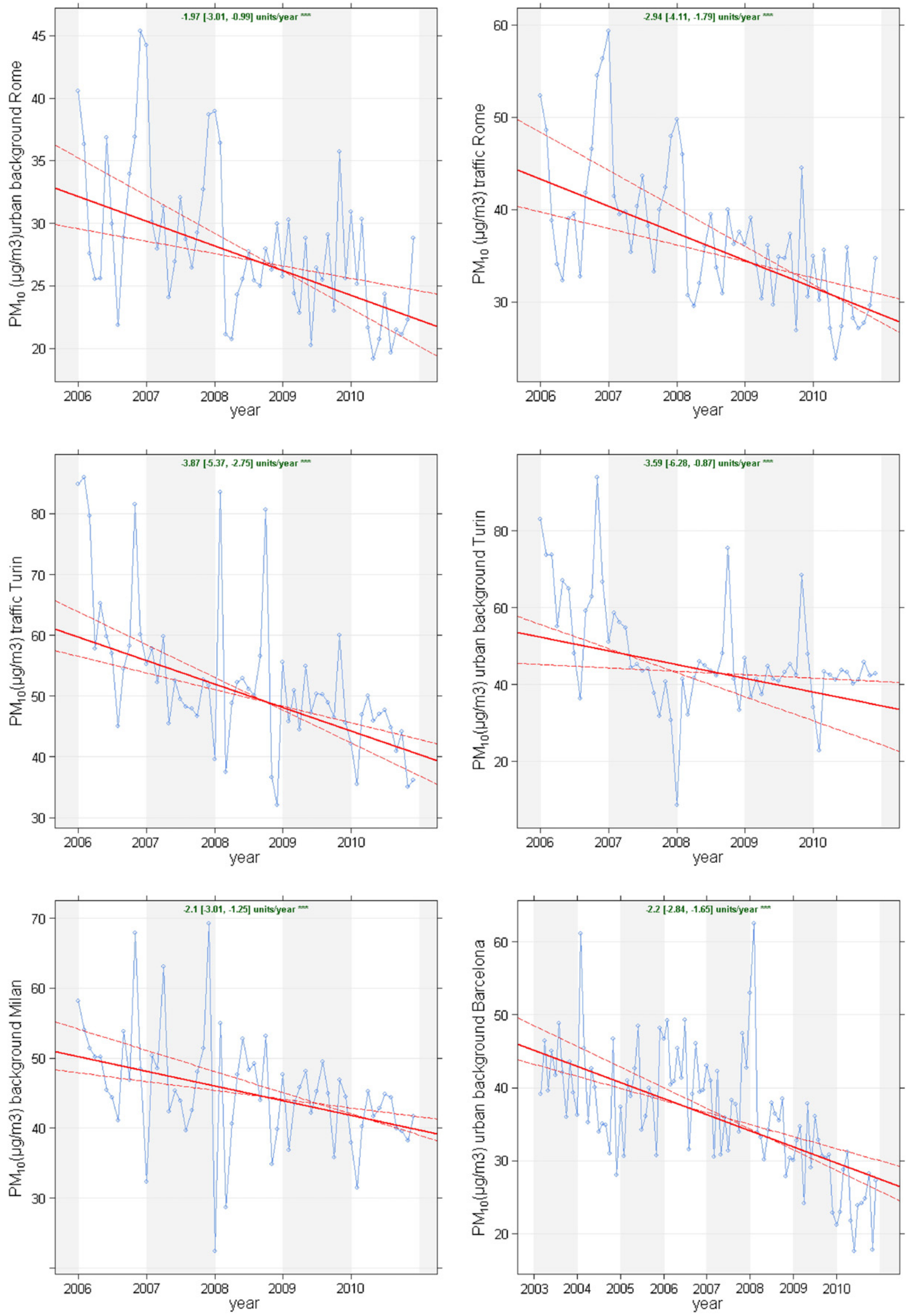

Fig. 9. Trend analysis of PM_{10}, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as $\mu g\ m^{-3}$ per year and the 95% confidence intervals in the slope. City and type of site are given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

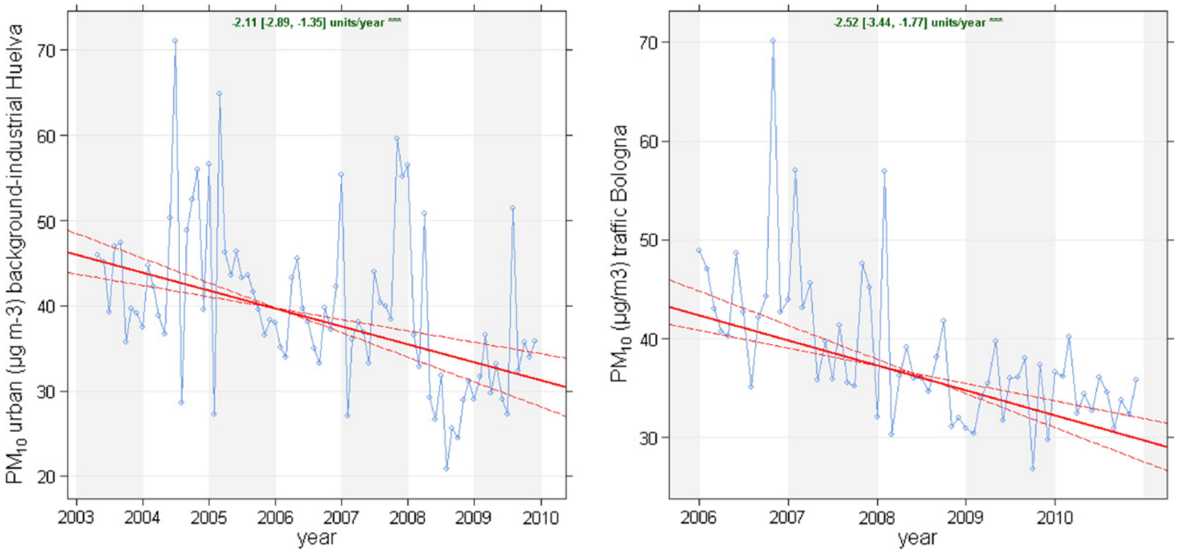

Fig. 9 (*continued*).

Euro 4 in 2005. The Euro 5 standard came into force on 2009, and required all new cars covered by the legislation to emit less particulates and nitrogen oxides than the limits set. The newest Euro 6, which will enter into force in 2015, will impose stricter limits on nitrogen oxides emitted by diesel engines. The significant emission reductions over the years were achieved with a combination of engine design optimization, availability of refined fuels, and the use of exhaust after treatment devices. Moreover the consequences of the economic crisis that affected Southern European countries should be taken into account as traffic intensity has been reduced (Cusack et al., 2012).

3.5. Seasonal pattern of air pollutants

NO_2, CO and O_3 presented the same temporal variation regardless of the type of site (traffic or urban background). O_3 had higher concentrations during warm months since its formation is favored during high solar radiation and temperature while for NO_2 and CO higher levels were observed during winter. SO_2 had two different temporal trends, in most sites SO_2 levels showed a small variability with slightly higher concentrations during summer (such as in Rome, Fig. 11) whereas in other cities (e.g. Madrid and Athens) in which fuel oil is used for heating, the trend was reversed with the higher values observed in winter months.

The seasonal variation of PM concentrations showed significant variability within the studied cities (see also the Supplementary material). The monitoring sites in Italy (Milan, Rome, Turin, Parma) had a remarkably identical temporal trend regardless of the type of the site, traffic or urban background site (Fig. 12 presents the temporal trend of PM_{10} and $PM_{2.5}$ in Rome for traffic and urban background sites; see also the Supplementary material). The highest concentrations of PM_{10} and $PM_{2.5}$ were observed during the cold months from November until March and the lowest ones during summer. The slight increase of PM_{10} and to a lesser extent of $PM_{2.5}$ concentration during the month of July in Rome is related to the occurrence of Saharan dust events (Perrino et al., 2009). The average value presented here is strongly influenced by the huge African dust events which occurred during the summer of 2006 and by minor events during 2010. In Madrid, the seasonal pattern of $PM_{2.5}$ was the same both in traffic and urban background sites (Fig. 13) with the lower concentrations observed during spring. However, for PM_{10} higher values were registered in the summer months but only in the background site.

3.6. Variation of air pollutant concentrations with wind direction and speed

The variation of the air pollutant concentrations with the wind direction and speed can help in investigating the source or origin and transport pattern of pollutants to the receptor. We examined the dependence of air pollutants on wind direction for the sites that were not influenced by street canyon effects. We also excluded the days that intense African dust intrusions were registered as these episodes increase significantly the dust load. Meteorological conditions were collected from stations close to the monitoring site. An example is given in Fig. 14 where the polar plots of gaseous pollutants and PM_{10} and $PM_{2.5}$ for the urban background site in Barcelona are shown (see also the Supplementary material).

The variation of SO_2, NO_2 and CO with wind speed and direction revealed the influence of local sources rather than regional contribution (see the Supplementary material). NO_2 and CO levels presented exactly the same pattern since road transport is thought to be the main emission source (Fig. 14). The main source of SO_2 in Barcelona is ship emissions from the busy port.

There was a remarkable consistency in the patterns in the traffic sites (also see the Supplementary material) with the highest concentrations of PM_{10} and $PM_{2.5}$ being detected under low wind speeds having a very local origin. In urban background site the concentrations were higher when the air masses come from the city center and major highways. In the case of Barcelona (Fig. 14) significant concentrations were clearly recorded towards the major traffic routes and the city center while the air mass transport from the coast (ship emissions) was also evident.

4. Conclusions

Previous studies reported significant variability of air pollutants across Europe with the lowest concentrations generally found in Northern Europe and the highest in Southern European countries. Within MED-PARTICLES project the concentrations levels of PM and gaseous pollutants were investigated in traffic and urban background sites in Southern Europe. The highest PM levels were observed in Greece and Italy (Athens, Thessaloniki, Turin and Rome) while all traffic sites showed high NO_2 levels, frequently exceeding the established limit value. As it was expected, concentrations at traffic sites were higher than those at urban background stations for all pollutants except for O_3. High $PM_{2.5}/PM_{10}$ ratios were calculated indicating that fine particles comprise a large fraction of PM_{10}, with the highest values found in the urban background sites. It

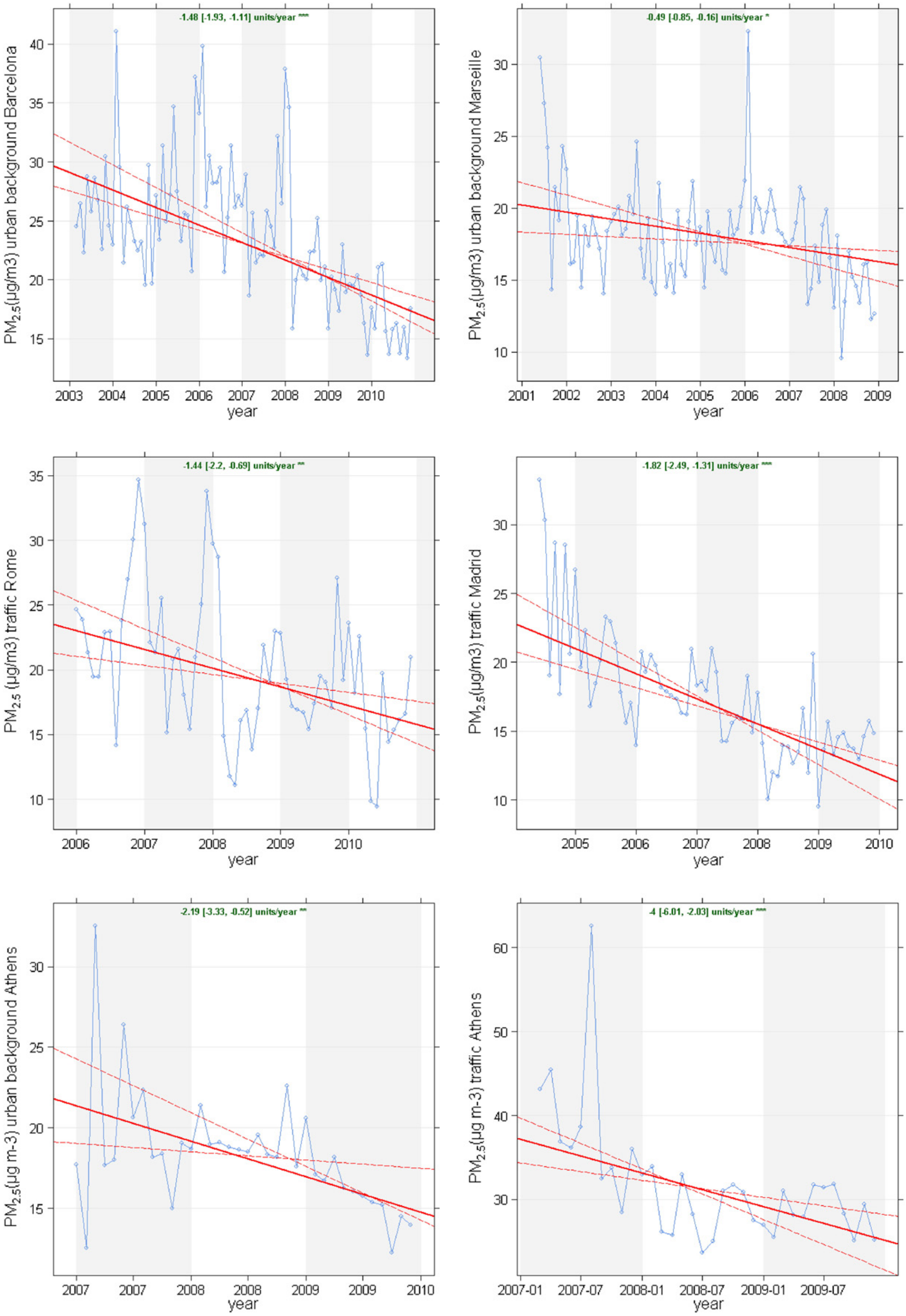

Fig. 10. Trend analysis of $PM_{2.5}$, for traffic and urban background sites in Southern Europe. The solid red line shows the trend estimate and the dashed red lines show the 95% confidence intervals for the trend. The overall trend is shown at the top-left as $\mu g\ m^{-3}$ per year and the 95% confidence intervals in the slope. City and type of site are given in the y-axis, *: the trend is significant to the 0.05 level, **: the trend is significant to the 0.01 level, and ***: the trend is significant to the 0.001 level.

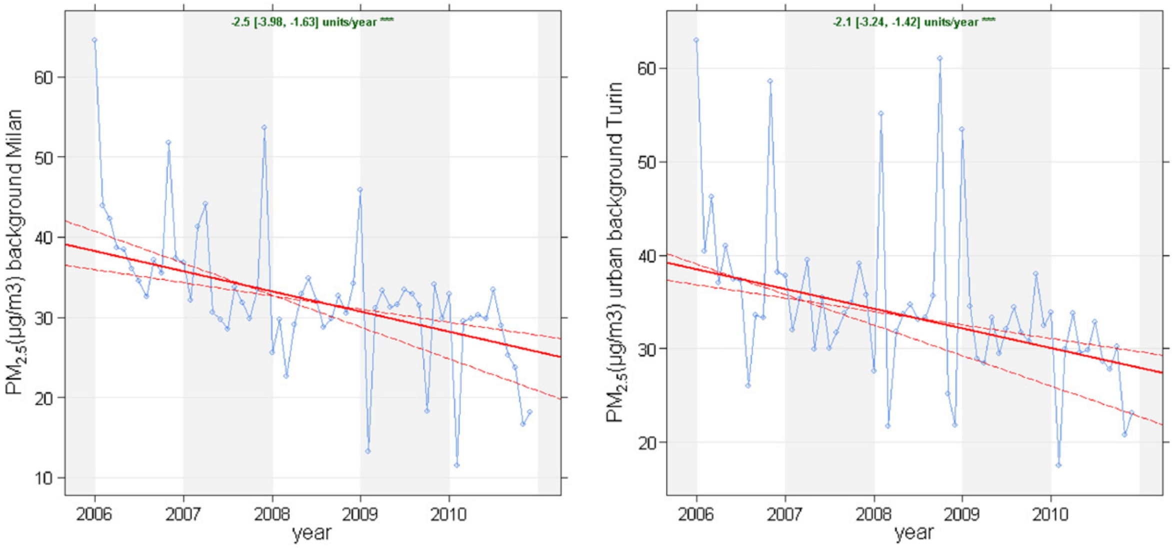

Fig. 10 (*continued*).

seems that although in traffic sites the concentrations of both $PM_{2.5}$ and PM_{10} are significantly higher than those registered in urban background sites, the coarse fraction $PM_{2.5-10}$ is more important at the traffic sites. This fact is probably due to the high levels of resuspended road dust in sites highly affected by traffic, a phenomenon especially relevant for Mediterranean countries. The long-term trends of air pollutants revealed a significant decrease of the concentrations levels for PM, SO_2 and CO due to the combination of EURO standards, the reduction of sulfur content in fuels, the engine design optimization, and the use of exhaust after treatment devices. On the contrary the implementation of the EURO standards had a smaller or no effect on NO_2 levels for which no clear trend or slightly increasing trends were observed. Beside the African dust intrusions that increase significantly PM_{10} mass levels (especially in the central and eastern Mediterranean Basin) the origin of air pollution in Southern Europe seems to be local rather than regional with the highest levels registered under low wind speeds.

Conflict of interest

The authors declare that they do not have any actual or potential financial and personal conflict of interests with other people or organizations.

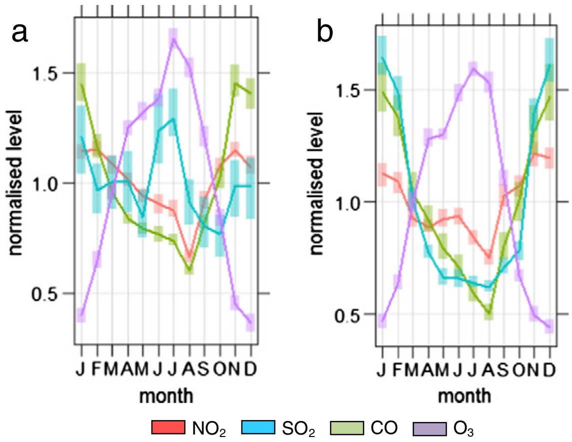

Fig. 11. NO_2, SO_2, O_3 and CO monthly variations in μg m^{-3} at a) traffic site in Rome and b) traffic site in Madrid.

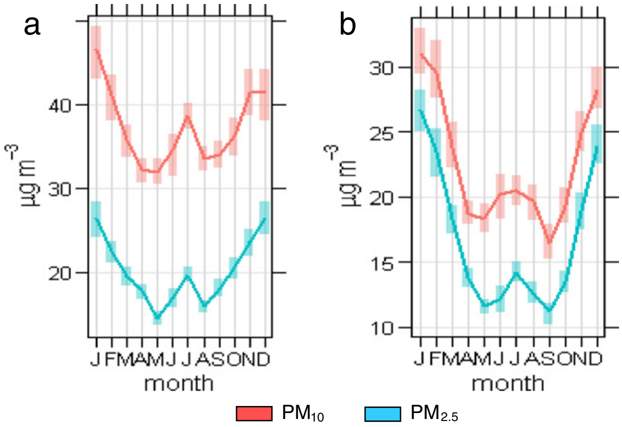

Fig. 12. PM_{10} and $PM_{2.5}$ monthly variations in μg m^{-3} at a) traffic site in Rome and b) urban background site in Rome for the period 2006–2010.

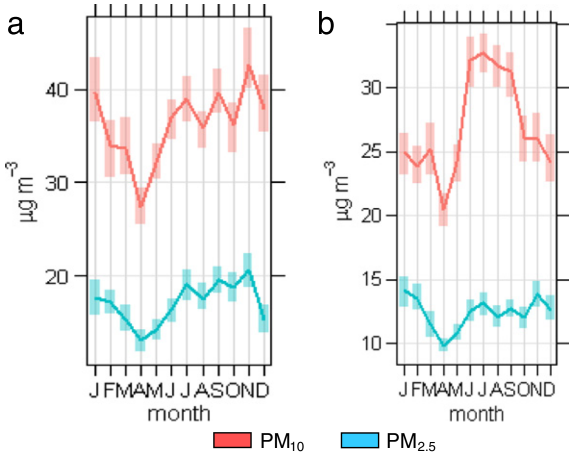

Fig. 13. PM_{10} and $PM_{2.5}$ monthly variations in μg m^{-3} at a) traffic site in Madrid and b) urban background site in Madrid for the period 2001–2009.

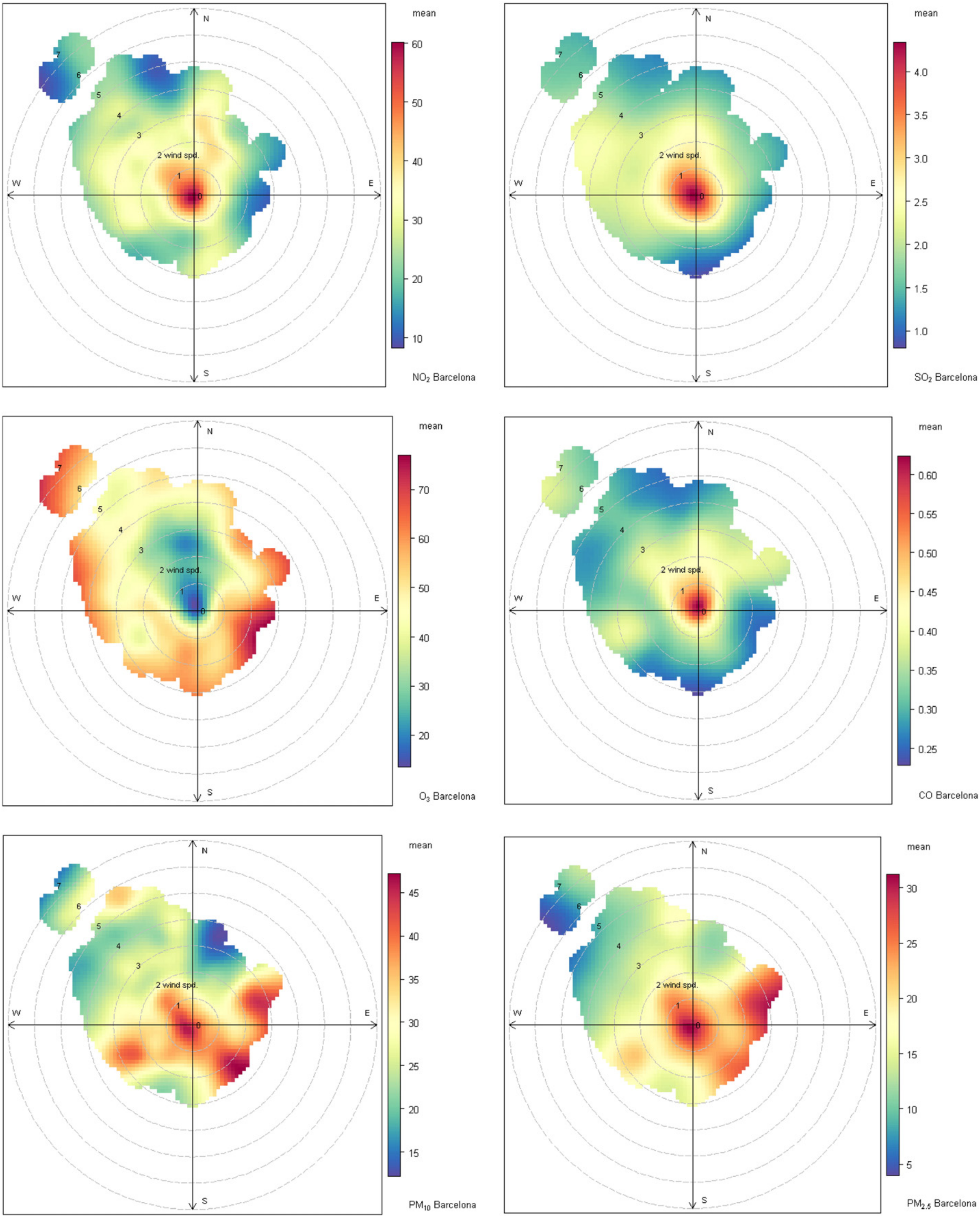

Fig. 14. Polar plots of SO_2, NO_2, O_3, CO, PM_{10} and $PM_{2.5}$ concentrations in Barcelona for the period 2003–2010.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.04.096.

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