Atmospheric Environment 132 (2016) 332–344

Contents lists available at ScienceDirect

Atmospheric Environment

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

Assessment of the variability of atmospheric pollution in National Parks of mainland Spain

M. Escudero [a, *], A. Lozano [a], J. Hierro [a], O. Tapia [a], J. del Valle [a], A. Alastuey [b], T. Moreno [b], J. Anzano [c], Xavier Querol [b]

[a] Centro Universitario de la Defensa (CUD) de Zaragoza, Academia General Militar, Ctra. de Huesca s/n, E-50090 Zaragoza, Spain
[b] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18-26, E-08034 Barcelona, Spain
[c] Laser and Environment Laboratory, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza, Spain

HIGHLIGHTS

- First comprehensive assessment of the levels of atmospheric pollutants in National Parks in Spain.
- Regional sources and the influence of transport scenarios affect pollutants levels in National Parks.
- Emissions patterns and changes in the PBL height explain seasonal variability of pollutants.
- Ozone exhibit high levels in National Parks increasing concentrations towards the east of Iberia.
- Analysis of daily variability reveal impact of anthropogenic sources in some parks.

ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form
17 February 2016
Accepted 4 March 2016
Available online 10 March 2016

Keywords:
O_3
NO_x
SO_2
PM_{10}
$PM_{2.5}$
National parks
Spain

ABSTRACT

Air quality in nine National Parks in mainland Spain was assessed analysing SO_2, NO_x, O_3, PM_{10} and $PM_{2.5}$ data from background stations. As emissions in and around parks are limited, the levels of primary pollutants are low. Concentrations of secondary pollutants are high especially in summer due to photochemical production. The geographical variability of pollutants responds to regional emission patterns and the dominant circulation regimes in different regions resulting in west-east gradients for O_3 and *PM*. Seasonal variability of pollutants was also interpreted in virtue of transport scenarios, changes in photochemical activity and emissions variability. NO_x and SO_2, maximize in winter due to higher emissions while O_3 and *PM* do it in summer due to photochemical production, lower precipitation and, in the case of *PM*, the occurrence of African dust outbreaks. The diurnal evolution was interpreted in virtue of variability in emissions and changes in the Planetary Boundar Layer height.

1. Introduction

Atmospheric pollutants are gases and particles present in the atmosphere which exert negative effects on health (WHO, 2006, 2008), climate (IPCC, 2013), ecosystems and vegetation (UNECE, 1988; Irwin et al., 2002; Fenn et al., 2003; Paoletti, 2006) and materials (Kucera and Fitz, 1995; de Leeuw, 2000; Screpanti and Marco, 2009). Regarding to their epidemiological and environmental effects, those classically monitored in air quality networks are sulfur dioxide (SO_2), nitrogen oxides ($NO_x = NO + NO_2$), ozone (O_3) and atmospheric particulate matter (*PM*).

Natural sources of SO_2 include volcanoes and terrestrial or oceanic biogenic sources that emit significant amounts of precursor species such as dimethyl sulfide ($(CH_3)_2S$) which interact chemically to produce SO_2 (Andreae and Crutzen, 1997) while anthropogenic sources are mainly related with the use of fossil fuels (coal, fuel oil or wood). In recent years in Europe and North America, there has been a clear reduction in the use of these fuels but they are still used in power stations, ships and aircraft engines and in the

* Corresponding author.
E-mail addresses: mescu@unizar.es (M. Escudero), xavier.querol@idaea.csic.es (X. Querol).

http://dx.doi.org/10.1016/j.atmosenv.2016.03.006
1352-2310/

residential sector (Querol et al., 2014). NO_x are generally emitted in combustion processes in the form of NO that, after interaction with other species such as O_3 and volatile organic compounds (VOC_s), is transformed to NO_2. The anthropogenic sources of NO_x include traffic, biomass burning and industry. Lightning, forest fires and bacterial processes in soils that convert ammonia (NH_3) into NO_x are the major natural sources. Ozone is a trace gas with secondary origin which, except for a small proportion coming from stratospheric intrusions, is formed in the troposphere by means of photochemical reactions involving NO_x and VOC_s (Atkinson, 2000). Finally, the atmospheric aerosols or PM are solid and liquid particles in the atmosphere with a wide variety of sizes, compositions and origins. Size is essential to evaluate PM toxicity because finer particles have a greater capacity to penetrate into the respiratory tract (Dockery et al., 1993). Following epidemiological criteria, two size fractions are generally monitored: PM_{10} and $PM_{2.5}$ (particles with less than 10 and 2.5 μm of diameter respectively). The heterogeneity of PM explains the large number of potential sources (EC, 2004). Oceans, soils, volcanoes and vegetation are major natural sources of primary PM and of gaseous precursors (SO_2, NO_x, COV_s, NH_3 among others). The main anthropogenic sources are traffic, industry, the residential sector and agricultural and livestock activities.

The National Parks (NP) are areas with significant natural and environmental features which are legally recognised by a nation in order to protect their resources and biodiversity with the objective of preserving them for future generations. The classification of a region as a NP represents the maximum figure of environmental protection granted in national legislation. In North America the importance of monitoring and controlling levels of atmospheric pollutants in National Parks has been largely recognised. Monitoring networks for different atmospheric parameters have been active for over 25 years (Percy and Karnosky, 2007) controlling gaseous pollutants such as SO_2, NO_x and O_3, speciation of PM and visibility and deposition. NP also implements field campaigns with the objective of obtaining a deeper insight on certain pollutants such as O_3 using passive samplers or mobile monitors and other photochemical oxidant pollutants. These data have been employed in a considerable number of research studies. The first efforts focused on the study of reactive gases (SO_2 and NO_x) and PM and their link with atmospheric visibility (Eatough et al., 1997; Pitchford et al., 2000; Malm et al., 2005; McMeeking et al., 2005; Engling et al., 2006). Excess nitrogen deposition in NP in the United States has been addressed by several authors (Burns, 2003; Fenn et al., 2003; Beem et al., 2010; Benedict et al., 2013; Ellis et al., 2013; Prenni et al., 2014) with emphasis on high elevated areas such as the Rocky Mountains. The variety of ecological effects of O_3 has motivated several studies (Temple, 1989; Ray, 2001; Burley and Ray, 2007; Preisler et al., 2010; Burley et al., 2014) highlighting the high levels of existing in the parks located at the western regions of the US and the important impact of wildfires increasing O_3 levels in NP (Preisler et al., 2010).

In Spain vigilance of air quality in the NP network has not been regular and has been mostly based on specific studies. Few studies have addressed changes in deposition in NP (Camarero and Aniz, 2010; García-Gómez et al., 2014; Barberán et al., 2014) revealing the importance of the monitoring of reactive nitrogen species because of the risk of exceedances of critical loads for different types of vegetation. Regarding pollutant gases, Sanz et al. (2007) conducted a study on O_3 levels in different NP based on dosimetry campaigns, Villanueva et al. (2014) studied the levels of ozone and VOC_s in Cabañeros NP while Adame et al. (2014) performed a complete field campaign of atmospheric photo-oxidants in Doñana NP. Finally, other studies have evaluated levels of PM components in particular NP such as Doñana (de la Campa et al., 2009; González-Castanedo et al., 2015). Despite these efforts, it is still necessary to make an assessment of the levels of air quality in NP in Spain to provide consistent and comparable information which allows the detection of the potential problems and environmental hazards associated with air pollutants. The main objective of this study is to conduct such assessment seeking to quantify and interpret the differences in pollutant levels in NP with different geographical locations and topographical features and to determine seasonal behavioral patterns of atmospheric pollutants.

2. Materials and methods

2.1. Stations and data representativity

One of the limitations for the planning of this study was the scarcity of long term data on air quality parameters available inside the NP of Spain. The main reason is that most of NP do not have access to the national electrical grid due to preservation policies. Therefore, an initial selection of stations belonging to operational air quality networks was made searching for regional background or remote sites which could assure the adequate representativity for the parks. Requirements such as maximum possible proximity to the NP (always <40 km and in most cases less than 20 km) and similarity with the nearby park in aspects such as environmental conditions, altitude and topography (Table 1) were imposed.

Different authors have performed studies to evaluate the representativeness for average measurements of rural stations as the ones used in this work. Larssen et al. (1999) offered a definition of the area of representativeness of a monitoring station as the region in which the concentration does not differ from the concentration measured at the station by more than a specified amount. Based on this definition, the authors estimate the radius of the area of representativeness for regional background stations ranges between 25 and 150 km while for remote stations it is 200–500 km. More recently, Henne et al. (2010) estimated the area of representativeness of rural stations for O_3, NO_2 and CO across Europe by evaluating the catchment areas for different advection periods. For the shortest advection period tested in that work (12 h), catchment areas with radii between 29 and 195 km were determined. Based on the relationship between annual concentrations of NO_2 with land use characteristics, Janssen et al. (2012) also found large areas of representativeness (radius >10 km) for rural stations in Belgium. Summarising, all these references demonstrate that the radius of the area of representativity of rural stations is larger than the distance from the NP and the sites selected for this study. Moreover, the analysis performed in this study deals with the average levels of pollutants and not with specific events of hourly or daily durations in which representativity is difficult to be assured. In consequence, it can assumed that the data employed in this study is closely indicative of the air quality standards in the NP.

Based on the data from the selected stations, 9 of the 10 NP located in mainland Spain (Fig. 1 and Table 1) have been characterised: Islas Atlánticas (IAT), Picos de Europa (PEU), Ordesa y Monte Perdido (ORD), Aigüestortes y lago de Sant Maurici (AIG), Sierra de Guadarrama (GUA), Monfragüe (MON), Cabañeros (CAB), Doñana (DON) and Sierra Nevada (SNE).

The features of the 9 NP analysed in this study present strong differences. Five of them are high-mountain ecosystems from which 3 are Atlantic (PEU, ORD and AIG) and 2 are Mediterranean (GUA and SNE), 2 more are located in Mediterranean medium-mountain terrain (CAB and MON) while IAT and DON represent low altitude terrestial-maritime and wetland ecosystems respectively. Although anthropogenic emissions from inside NP are practically non-existent, external sources located in the

Table 1
Monitoring stations and their related NP employed in this study.

Station code	Name	Network	Lat. (° N)	Long. (°E)	Alt. (m.a.s.l.)	Nat. Park (dist.)	Data
ES0005R	Noia	EMEP	42.72	−8.92	685	IAT (~20 km)	SO_2, NO_x, O_3, PM_{10}
ES1989A	Lario	Castilla y León	43.04	−5.09	1140	PEU1 (~15 km)	SO_2, NO_x, O_3
ES0008R	Niembro	EMEP	43.44	−4.85	115	PEU (~17 km)	SO_2, NO_x, O_3, PM_{10}, $PM_{2.5}$
ES1883A	Torrelisa	Aragón	42.46	0.18	1005	ORD (~10 km)	SO_2, NO_x, O_3, PM_{10}
ES1982A	Montsec	Catalunya + IDAEA-CSIC	42.05	0.73	1570	AIG (~40 km)	SO_2, NO_x, O_3, PM_{10}, $PM_{2.5}$
ES1802A	El Atazar	Madrid	40.91	−3.47	940	GUA (~20 km)	SO_2, NO_x, O_3, PM_{10}, $PM_{2.5}$
ES0001R	SP de los Montes	EMEP	39.55	−4.35	917	CAB (~15 km)	SO_2, NO_x, O_3, PM_{10}, $PM_{2.5}$
ES1616A	Monfragüe	Extremadura	39.85	−5.94	376	MON (−)	SO_2, NO_x, O_3, PM_{10}
ES0017R	Doñana	EMEP	37.05	−6.56	5	DON (~1 km)	SO_2, NO_x, O_3, PM_{10}
ES0007R	Víznar	EMEP	37.24	−3.53	1230	SNE (~10 km)	SO_2, NO_x, O_3, PM_{10}, $PM_{2.5}$

surroundings can be relevant in some cases. Important cities are present near IAT (Vigo), GUA (Madrid and Segovia), DON (Seville, Huelva, Jerez de la frontera and Cádiz) and SNE (Granada). Regarding traffic sources, major roads run in the vicinity of GUA, DON, SNE and PEU while important industrial estates can be found in Huelva and Gibraltar which may influence Doana NP air quality.

The parameters used in this study are regularly monitored in air quality stations (SO_2, NO_x, O_3, PM_{10} and $PM_{2.5}$). Data was collected making use of standard methods as reflected in the EU Directive 2008/50/EC: SO_2 was measured by UV fluorescence, NO_x by chemiluminescence and O_3 by UV photometry in the three cases by means of automatic monitors. Daily data of PM_{10} and $PM_{2.5}$ were obtained by the standard gravimetric method in all cases except in El Atazar where automatic equipment based on β attenuation was used applying a correction factor of, obtained after intercomparison with the gravimetric method (1.0 for 2008–2010 and 0.73 for 2011–2012). Complete time series from 2008 to 2012 were always available except in Montsec where monitoring began in 2010. High data availability was obtained in all cases (>90% for automatic data and >80% for *PM*). A particular consideration on the characteristics of NO_x and SO_2 monitors must be mentioned here since trace level analyzers were available in all the stations with the exception of Lario, Torrelisa, El Atazar and Monfragüe. The detection limit of a regular monitor is around 0.5 ppb (equivalent to 1.31 $\mu g/m^3$ for SO_2 and 0.94 $\mu g/m^3$ for NO_x), approximately one order of magnitude higher than in trace level ones. When ambient concentrations are below detection limit (a situation that can often occurs in background stations), the measurement is usually set at a fixed level generally corresponding to 50% of the detection limit, generating an upward bias in stations equipped with regular monitors with respect to those with trace level devices.

2.2. Meteorological analyses

In order to characterise the origin of air masses, 48-h back-trajectories were computed once a day for the period 2008–2012 for each NP with HYSPLIT4 (Draxler and Hess, 1998) model using GDAS 0.5-deg meteorological data. Clustering analyses of the back-trajectories were also performed with HYSPLIT4 to quantify the occurrence of transport regimes over each NP. A similar clustered

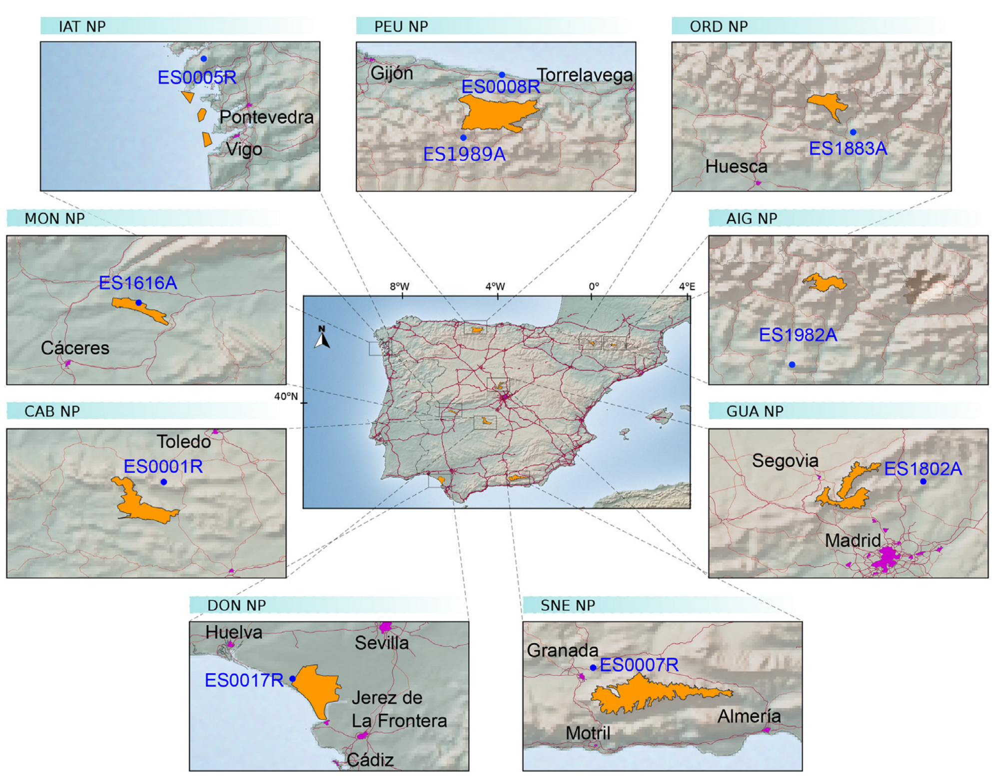

Fig. 1. Location of the NP and the monitoring stations used in this study.

trajectory analysis was employed before for characterising atmospheric transport in three NP in western US in a study by Hafner et al. (2007). In this work it was demonstrated that the prediction of precipitation and fine particle concentrations in remote areas improved for short period trajectory clustering with respect to longer periods. This result suggests that the chosen 48-h clusters are adequate although the importance of long range transport can be slightly underestimated.

An analysis of planetary boundary layer (PBL) heights, every 3 h, was also performed. It should be noticed that GFS/GDAS code suffered a major upgrade on July 27th 2010, which corresponds to the studied period. This upgrade affects the reported values of PBL heights, with a clear reduction in maximum PBL heights after the upgrade, in all the studied locations. This lack of homogeneity in the available GDAS PBL heights is the reason why ERA-Interim data with 0.75-deg resolution were used as a source of PBL heights instead of GDAS 0.5-deg data. Nevertheless, a comparison between PBL heights as obtained from ERA-Interim and GDAS during the period considered was checked in Fig. 2 for four specific locations: Doñana (ES0017R) which is close to sea in the south of the Iberian Peninsula, Víznar (ES0007R) which is a southern mean mountain location, Montsec (ES1982A) which is a northern mean mountain location and Monfragüe (ES1616A) which lies in a southwestern hilly area. A simple moving average of the PBL height at 15:00 UTC was obtained from a 29 days sample centered on the considered date; during the first and the last period of 29 days the sample was truncated so as to fit into the 2008–2012 period .[1]

An analysis of Fig. 2 reveals the reduction of PBL GDAS heights after the code upgrade. In locations where GDAS data were higher than ERA-Interim data, this reduction has improved the agreement between both data sources; however, in locations where GDAS data was either lower or similar to ERA-Interim data before the upgrade, this reduction has increased the discrepancies between both sources. The particular case of Víznar would be worth of a more refined study.

3. Results

3.1. Average levels

Due to the their distant location from major sources, the average concentrations of primary pollutants in the NP are low (Fig. 3 and Table 2). This occurs for SO_2 with mean levels in the range 1–2 $\mu g/m^3$. However, differences are observed between the stations equipped with trace level analyzers (0.44–1.08 $\mu g/m^3$) and the rest, equipped with regular monitors (1.55–2.28 $\mu g/m^3$) reflecting the upward bias of regular monitors explained above.

Average NO_x levels in the study period ranged between 1.9 and 9.3 $\mu g/m^3$ with the highest concentrations in MON, ORD and GUA although in these sites it may be reflected again the use of regular analyzers with higher detection limits. The proximity to traffic ways has a clear impact on NO_x concentrations as observed in DON, SNE or PEU (5.2–6.3 $\mu g/m^3$) compared with sites located further from important roads such as CAB, IAT or AIG (1.9–3.4 $\mu g/m^3$). Moreover, in the case of PEU the presence of power plants in the region may also increase NO_x levels (Querol et al., 2014).

The Directive EU/50/2008 establishes critical levels for protection of the vegetation for SO_2 (20 $\mu g/m^3$ for both the of the annual and winter period averages) and NO_x (30 $\mu g/m^3$ for the annual mean) that were not surpassed during the study period in the analysed sites.

PM_{10} and $PM_{2.5}$ concentrations ranged in 7–19 $\mu g/m^3$ and 6–11 $\mu g/m^3$ respectively. The highest levels corresponded to locations eventually affected by anthropogenic sources such as densely populated areas as Madrid (GUA) and Granada (SNE), or important traffic ways like PEU and DON. The impact of African dust intrusion may also increase PM levels especially is southern areas as SNE. The remaining stations are less exposed to anthropogenic emissions and, consequently, present lower PM levels.

As it is the case of other rural areas across the Mediterranean basin (Sicard et al., 2013), mean O_3 levels in the analysed stations reached considerable values in the study period (61.7–89.5 $\mu g/m^3$). The strong emissions of precursors occurring in the highly industrialised and populated Mediterranean flank help to increase O_3 levels in this area (73.9–89.5 $\mu g/m^3$) in contrast with western Iberia (61.7–72.0 $\mu g/m^3$) although climatic effects also are important.

Apart from the variability associated with emission patterns, climatic conditions are essential to an understanding of the spatial changes in pollutants levels. The atmospheric circulation over each NP has been studied considering five source areas: Atlantic Ocean (ATL), European Continent (EU), Mediterranean Sea (MED), Northern African Continent (NAF) and Iberian Peninsula (PIB). As shown in Fig. 4, the transport of Atlantic air masses was the most common situation in all NP but the frequency was higher over west of the PIB (53–80% of the days) than in the remaining NP (30–51%). ATL episodes imply the arrival of clean oceanic air masses sometimes with precipitation associated with frontal systems. This generate ventilation and, in occasions, atmospheric wash-out.

PIB events occur when lack of prevalent advective conditions were observed. Typically, anticyclonic conditions over the Iberian Peninsula give rise to this scenario and, in consequence, precipitation is scarce. During winter PIB episodes, near-ground inversion layers develop leading to the accumulation of pollutants in urban and industrial locations. Summer PIB episodes are generated by the displacement of the Azores high over the western Mediterranean basin and the development of a thermal low over the central plateau of the Iberian Peninsula. The convergence of winds from the coastal areas, through natural passes, towards the centre of the Peninsula (Millán et al., 1996) and the enhanced mesoscale circulation yield to recirculation and aging of air masses. As shown in Fig. 4, PIB transport is frequent over NP at eastern and central Iberia (33–48% of the days), and less frequent over northern and western parks (14–26% of the days).

EU transport is rare in parks located in the centre, east, southwest and southeast (1–5% of the days) and more frequent in those located near the European continent (7–13% of the days). MED episodes are less frequent in northern NP (1–9%) than in southern ones (11–19%) mainly because the same synoptic situations inferring EU transport over the north often generate MED events at the southern part of the peninsula. Precipitation is common under MED transport due to the moist character of Mediterranean air masses.

The occurrence of NAF episodes increase in frequency from north to south and from west to east (3–5% on the south and the east, and 1–2% on the north). These proportions are low compared with previous studies (Escudero et al., 2005; Pey et al., 2013) due to two main reasons. Firstly, in order to avoid excessive computational effort in the clustering analyses, 48-h back-trajectories have been computed so long range transport such as NAF can be underestimated. Secondly, the origin of air masses has been elucidated here exclusively from back-trajectories clustering while in previous studies sources of information such as model outputs or satellite imagery were used for detecting dust.

O_3 and, in a lesser extent, PM show a west-east gradient closely related with the variability of the occurrence of ATL episodes and opposite to the variability of the occurrence of PIB events. The greater ventilation and precipitation provided by ATL transport in

[1] It means, for instance, that the first value is the moving average of the 15 first days, whereas the last value in the moving average of the 15 last days.

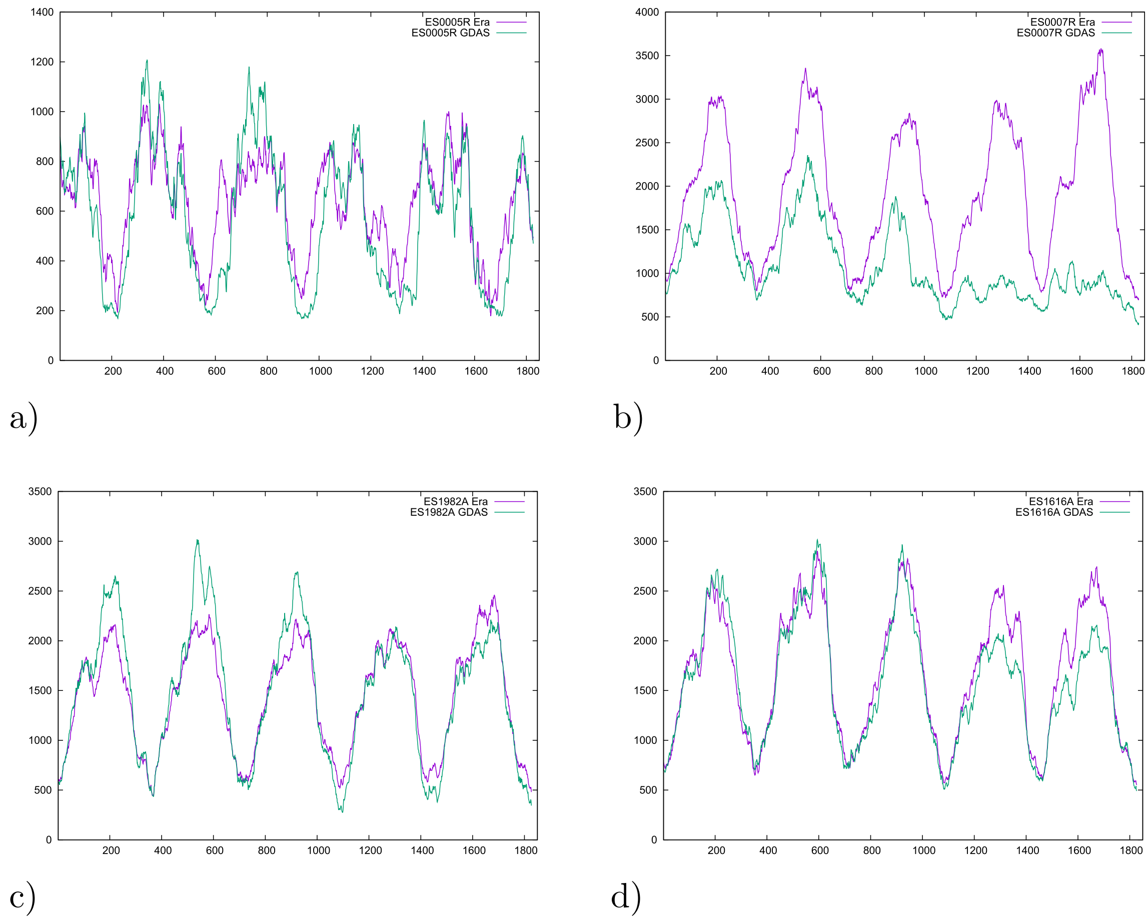

Fig. 2. Number of days since Jan 1st, 2008 in the *X* axis versus moving average of PBL height at 15:00 UTC, *Y* axis, in four locations: a) DON, b) SNE, c) AIG and d) MON. The reported value of PBL height is a simple mean of the actual values during the 29 days centered around the considered date, at 15:00 UTC every day. ERA-Interim values versus GDAS ones.

the western flank of the Iberian Peninsula help to keep *PM* and O_3 lower than in oriental and central areas. In DON, *NO* emissions from the industrial estates located near this NP may have resulted in lowering O_3 levels. Moreover, the specific orography of the eastern side of the Iberian peninsula characterised by mountain ranges parallel to the coast interspersed by valleys, generates regional circulation and aging of air masses resulting in elevated O_3 and *PM* levels (especially the secondary fraction) in background locations (Millán et al., 1996; Rodríguez et al., 2002). Finally, the higher frequency of NAF episodes in south and eastern NP contribute to increase *PM* levels in those parks (Escudero et al., 2005, 2007).

3.2. Seasonal variability

The seasonal variability of pollutant levels in NP (Fig. 5) was associated with emission patterns and with changes in ambient conditions. The concentrations of certain pollutants, such as SO_2, exhibit very low variability between summer-spring and autumn-winter. Only in some NP (PEU and IAT) light winter increases were observed associated with greater emissions from the residential sector and coal power plants.

NO_x concentrations showed higher levels in autumn-winter (20–60% higher than in spring-summer). Winter maxima reflect the increment of emissions with respect to summer months. In addition, the reduced photochemical activity during winter results in lower NO_2 destruction by photolysis. Finally, lower O_3 concentrations during autumn-winter also inhibits the elimination of *NO* by tritation. Exceptions were found in ORD, DON and SNE where maxima in summer is probably associated with an regional increment in traffic during summer vacations.

O_3 levels present strong spring-summer increases associated with enhanced photochemical activity. Average concentrations in early spring (March), are comparable to summer levels in most NP. Western parks (IAT, PEU and DON) show maxima in April decreasing slightly during summer linked with an earlier decline of solar radiation in that sector than in the remaining NP where maxima concentrations are observed during summer (CEAM, 2014).

The highest PM_{10} and $PM_{2.5}$ levels in NP are generally recorded in spring-summer but the differences between summer and winter are greater in PM_{10}. Spring-summer concentrations increase in 20–80% for PM_{10} and 10–40% for $PM_{2.5}$, with the weakest increments being registered in the northwestern locations (IAT and PEU). This is explained by the greater frequency of African dust intrusions over the Iberian Peninsula (Escudero et al., 2005, 2007), the lower precipitation reducing atmospheric washout and favouring *PM* resuspension, the enhanced photochemical production of secondary aerosols and the stronger vertical development of the mixing layer which eases the arrival towards NP of pollutants emitted in urban and industrial spots. Another maximum, secondary in the case of PM_{10} but of the same importance or even greater than the spring-summer peak for $PM_{2.5}$, is observed in February–March. These late winter maxima are associated with two processes. Firstly, the effect of winter African dust intrusions over the Iberian Peninsula with a outstanding impact on *PM* levels because, contrarily to summer African dust events, transport occurs

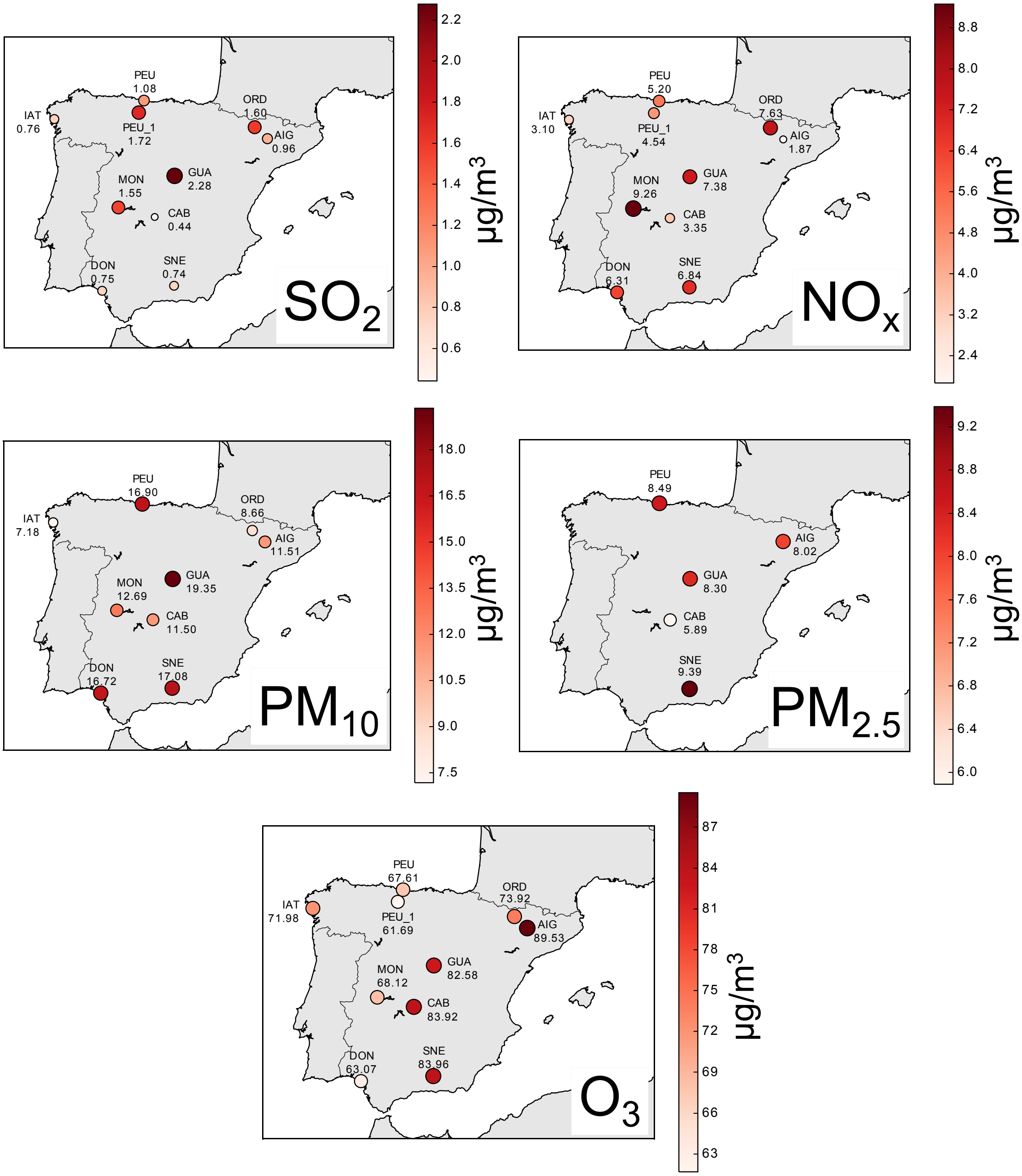

Fig. 3. Average levels of atmospheric pollutants in NP of mainland Spain for the period 2008–2012.

at surface level (Escudero et al., 2005). Moreover, the occurrence of anticyclonic situations in late winter with enough radiation may activate mountain breezes facilitating the arrival of pollutants to natural areas (Pey et al., 2010). These two processes combined with the milder summer conditions in northwestern NP (PEU and IAT) explain why average winter concentrations are higher than in summer in those sites.

3.3. Daily variability

One of the key parameters to understand the variability of the levels of pollutants during the day in remote areas is the evolution of the altitude and stability of the PBL. A strong vertical development of an unstable PBL aided by the enhancement of coastal and mountain breezes (Pey et al., 2010) facilitate a rapid transport of pollutants from urban and industrial areas towards rural sites. An unstable PBL may be decomposed into three sublayers: a surface layer, the lowest part of the PBL where averaged winds show a logarithmic profile versus elevation above the surface with strong turbulence production, a mixed layer, the core zone of the PBL where meteorological variables are well mixed and turbulence decays, and an entrainment or inversion layer, a transition zone between the PBL and the free troposphere where there is a mixture of air masses coming from both zones accompanied by strong variations of the meteorological variables.

Before realizing any analysis based on the height and stability of the PBL, it should be pointed out that there is not a unique definition of these properties. With regard to the estimation of the PBL

Table 2
Average, standard deviation and percentile of the concentrations of SO_2, NO_x, O_3, PM_{10} and $PM_{2.5}$ for the period 2008–2012 in the 10 monitoring stations used in this study.

		ES1989A-PEU	ES0008R-PEU	ES1802A-GUA	ES1616A-MON	ES0001R-CAB	ES1883A-ORD	ES0017R-DON	ES0005R-IAT	ES1982A-AIG	ES0007R-SNE
SO_2	Mean	1.72	1.08	2.28	1.55	0.44	1.60	0.75	0.76	0.96	0.74
	Std	2.05	1.61	1.51	1.49	0.57	1.62	1.13	1.42	1.16	0.98
	P90	3.80	2.19	4.00	3.56	0.82	4.00	1.47	1.78	2.20	1.63
NO_x	Mean	4.54	5.20	7.38	9.26	3.35	7.63	6.31	3.10	1.87	6.84
	Std	10.10	4.83	8.42	6.53	3.28	4.99	5.91	3.17	1.35	9.92
	P90	14.00	10.54	12.00	15.65	6.31	13.44	13.17	6.17	3.30	15.00
O_3	Mean	61.69	67.61	82.58	68.12	83.92	73.92	63.07	71.98	89.53	83.96
	Std	23.75	18.07	25.15	30.11	20.70	20.49	28.56	22.54	18.83	19.83
	P90	91.00	91.14	114.00	107.60	111.30	102.00	100.20	99.36	116.00	109.80
PM_{10}	Mean	–	13.35	19.32	–	–	13.35	–	–	–	–
	Std	–	8.15	13.10	–	–	8.15	–	–	–	–
	P90	–	22.21	34.00	–	–	22.21	–	–	–	–
$PM_{2.5}$	Mean	–	7.89	8.28	–	–	7.89	–	–	–	–
	Std	–	4.12	5.45	–	–	4.12	–	–	–	–
	P90	–	12.95	15.00	–	–	12.95	–	–	–	–

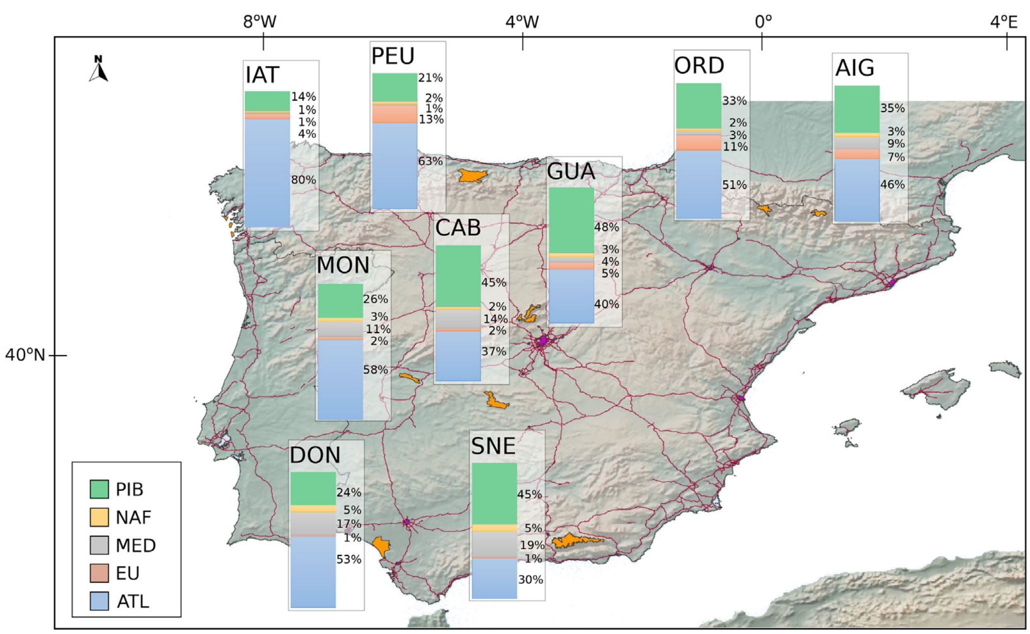

Fig. 4. Proportion of air mass transport scenarios over NP in mainland Spain based on clustering 48-h back-trajectories at surface level in the period 2008–2012.

height, see for instance (Seidel et al., 2012) and references therein, where ten different definitions were compared. Concerning the stability of the PBL, most studies are based on either the bulk Richardson number at the surface layer, or the Obukhov length (which is related to the height at which the TKE production of turbulence because of buoyancy equals its production because of shear flow), or the value of the surface heat flux (Zhang et al., 2014). In this work, PBL height values were taken from ERA-Interim data. According to the documentation of the IFS/ECWMF numerical code, the PBL height is defined as the level where the bulk Richardson number, based on the differences between quantities at that level and the lowest model level, reaches a critical value of 0.25. The definition is a slight modification of the one proposed by (Troen and Mahrt, 1986): virtual dry static energy is used instead of virtual potential temperature.

With regard to the stability criterion, IFS/ECWMF uses the sign of the Obukhov length, $L_O<0$ for unstable conditions, $L_O>0$ for stable conditions and $L_O=0$ for neutral conditions. In its turn, the sign of the Obukhov length is the opposite of the sign of the virtual temperature flux, see eqn. (1), in the surface layer, where positive flux is assumed to go upwards. The virtual temperature flux depends on heat and humidity fluxes and it may go to zero only if there is not momentum flux. Heat and momentum fluxes are provided by ERA-Interim.

$$Q_{0v} = \frac{J_{sh}}{\rho C_p} + \varepsilon T_n \frac{J_{lh}}{\rho L_v} \tag{1}$$

where J_{sh} is the sensible heat flux, J_{lh} is the latent heat flux, ρ is moist air density, C_p is the heat capacity at constant pressure for dry air, $\varepsilon \approx 0.6063$ is a constant used to compute virtual temperatures, T_n is an absolute reference temperature taken at a point close to the surface (T at 2m of elevation is provided by ERA-Interim) and L_v is the latent heat of vaporization of water. Since, the sign of Q_{0v} is the only relevant quantity, one may simply check the sign of $\rho Q_{0v} = (J_{sh}/C_p) + \varepsilon T_n (J_{lh}/L_v)$ without the need to compute air density near surfaces.

Fig. 6 shows the average diurnal cycle of the PBL height for each month in the studied NP for 2008–2012. Every diurnal cycle is divided into eight steps with a 3 h separation between them. PBL altitude maximizes in all sites around 15 h UTC coinciding with the maximum surface warming. Three different groups of sites can be

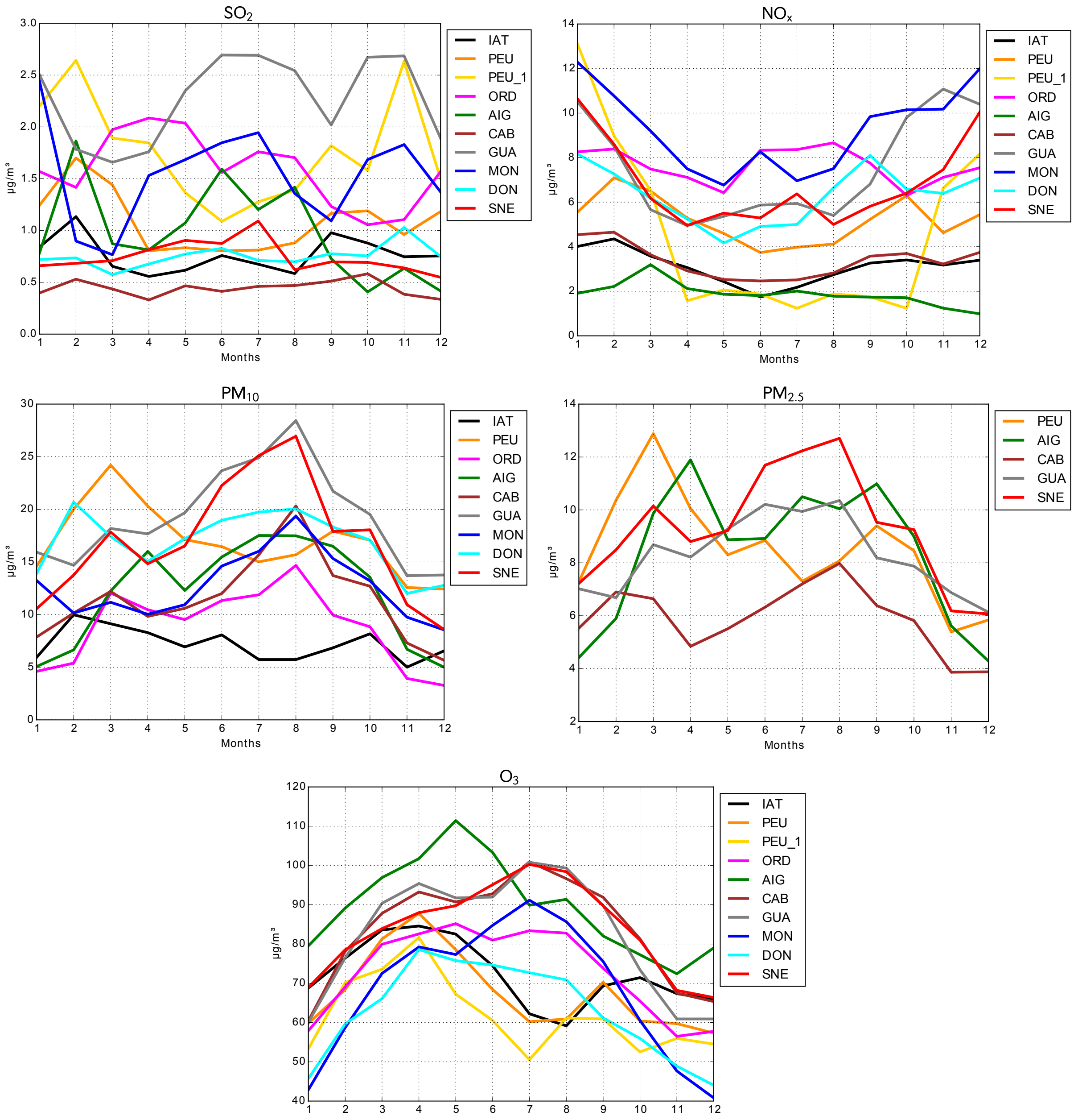

Fig. 5. Monthly mean concentrations of atmospheric pollutants in NP of mainland Spain for the period 2008–2012.

differentiated regarding the PBL daily cycles. In coastal locations (IAT, DON and PEU1), the influence of marine winds, intensified in the warm season, limits the vertical extent of the PBL. In continental locations in the North of the Iberian Peninsula (PEU, ORD and AIG), the PBL has a strong development in spring-summer reaching averages around 2000 m. This effect, which is due to an intense surface heating in peninsular areas isolated from maritime influence, is even stronger in continental locations in the South and the Center of the Iberian Peninsula (MON, GUA, CAB and SNE) with averages above 2500 m. During the cold season the vertical extent of the mixing layer is lower due to the reduced surface heating (maximum averages between 500 and 1000 m) and the main difference between continental and coastal sites is the much lower amplitude of the diurnal cycle in coastal sites.

This average behaviour of the PBL can be affected sporadically during African dust outbreaks as explained by Pandolfi et al. (2014). According to these authors, the PBL height decreases during African dust episodes due to two major factors related with the presence of the dust layer. Firstly, the decay in incoming solar radiation by dispersion and backscattering caused by mineral aerosols and the generation of a low-level inversion layer at the altitude where the African dust layer ends. Nevertheless, this a phenomenon that takes place under the influence of African dust transport which, as detailed above, is not dominant among transport scenarios so the actual impact on the average behaviour of the PBL (which is analysed in this paper) is not expected to be decisive.

Fig. 7 shows the diurnal cycle of the probability that the PBL be unstable for each month in three selected stations (DON, AIG and SNE) during the studied period with a 3 h time step. No more locations were selected because inland sites showed an intermediate

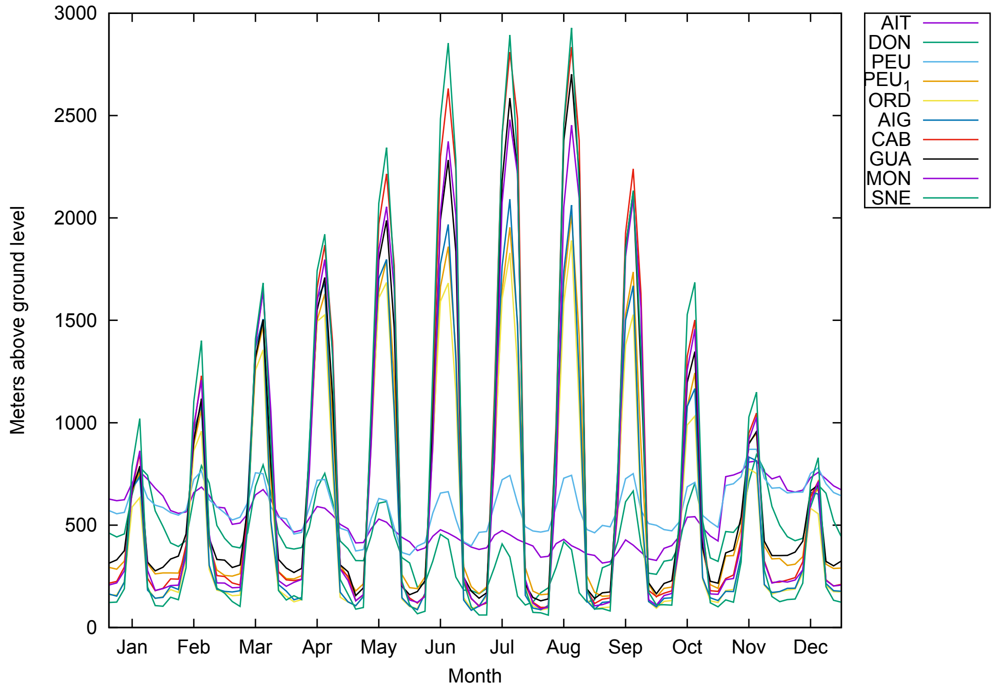

Fig. 6. Mean daily cycles of the PBL height for each month in NP of Spain during the period 2008–2012.

behaviour between that of SNE and that of AIG, whereas coastal locations behaved like DON. For a given location, month and hour, the distribution of the stability is rather sharp: there is a clear dominance of one of the two conditions and transitions towards the opposite situation are fast. The most striking feature is the high probability of stable conditions during the central hours of the day in coastal locations. The reason being that the sea surface keeps much cooler than the surrounding air what enforces a net sensible heat flux directed downwards (towards the sea) which is associated with the formation of a stable PBL. In the morning and in the late afternoon, differences of temperature between the sea and the surrounding air layer are not so high and the PBL turns unstable. An analysis of momentum fluxes revealed that there were no exact neutral conditions in any studied point at any considered time.

Fig. 8 shows the average daily cycles of the concentrations of pollutants separately for winter (October–March) and summer (April–September). SO_2 levels increase slightly in the central hours of the day although levels are really close to detection limit so those increments are in the same order of measurements errors. These midday increases are also detected in NO_x concentrations and may

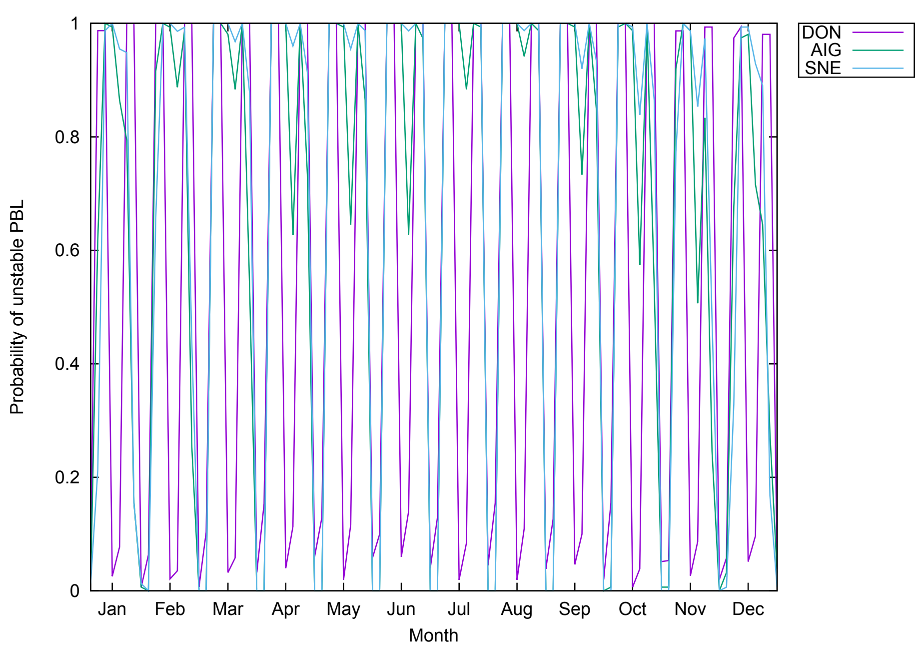

Fig. 7. Mean daily cycles of the probability that the PBL be unstable for DON, AIG and SNE during the period 2008–2012.

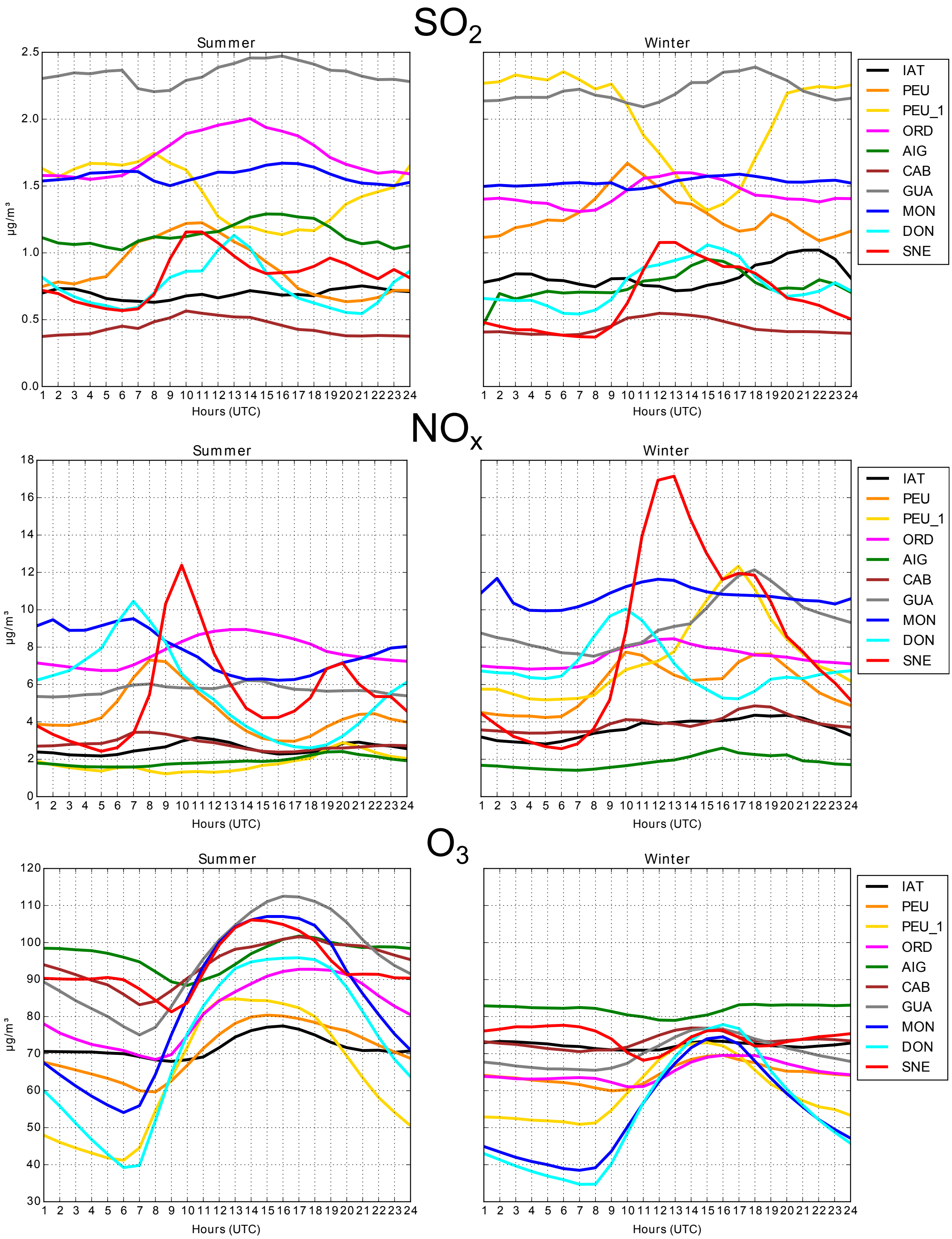

Fig. 8. Winter and summer mean daily cycles of the concentrations of gaseous pollutants in NP of Spain for the period 2008–2012.

be associated with the PBL height evolution presented above. The development of an unstable PBL with increasing altitude at the central hours facilitates the transport of pollutants from urban and industrial areas towards background regions which lie in the direction of the prevailing winds at the top of the PBL. In some parks (SNE, PEU and DON) two NO_x maxima are observed one in the morning and another in the evening. These are associated with traffic emissions in the rush hours indicating exposure to traffic sources due to the proximity to major roads or cities. Other stations (ORD, GUA or AIG) just present a single peak in the concentrations of NO_x during the afternoon. The direct impact of traffic sources on these sites is limited so it is the development of the PBL which progressively allows the arrival of well mixed air masses loaded with NO_x giving rise to a single concentration maximum.

The diurnal evolution of NO_x also present seasonal differences. As stated before, winter levels are higher than summer

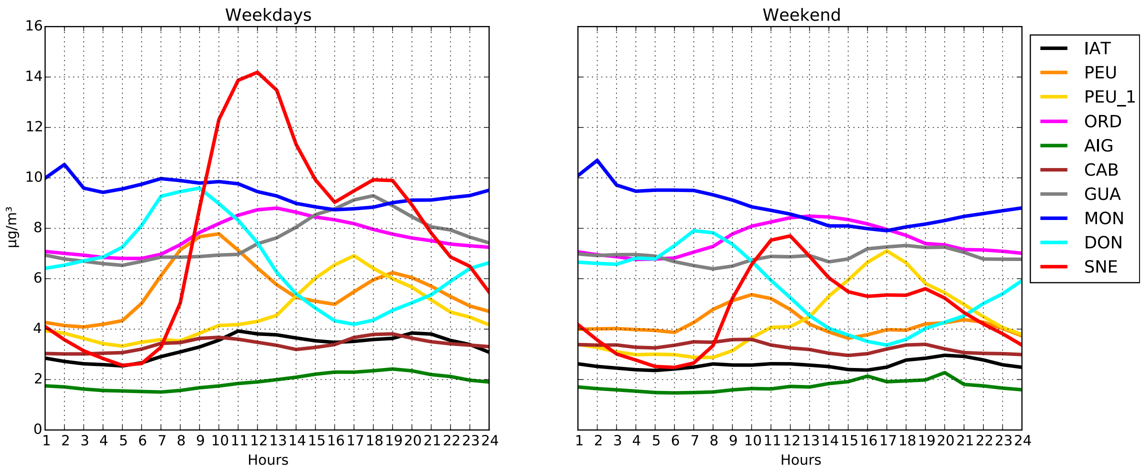

Fig. 9. Weekdays and weekends mean daily cycles of NO_x concentrations in National parks of Spain for the period 2008–2012.

concentrations due to three major factors associated with wintertime: Higher emissions, reduction in the photochemical activity which inhibits NO_2 photolysis and the reduction of NO titration limited by low O_3 concentrations. Another noticeable feature is that, in the sites where two daily maxima are detected, the morning peak occurs earlier during spring-summer than during autumn-winter. The stronger vertical extent of the PBL in summer along with the intensification of mountain breezes cause by higher temperature and radiation, facilitates the rapid arrival of NO_x from emission sources to the natural areas while in winter a more limited and slower growth of the mixing layer, which may be absent under thermal inversion conditions, delays the arrival of NO_x.

The mean daily cycles of NO_x have also been studied disaggregating weekdays from weekends (Fig. 9). This approach was used in Escudero et al. (2014) in order to discriminate the impact of anthropogenic activity on the levels of NO_x given that emissions derived from human activities fall drastically during weekends. In some NP (PEU, GUA, DON and SNE) present NO_x increments in weekdays with respect to weekends. These are especially relevant in the hours when concentrations reach their maximum values in the central hours or during rush hours. This must be interpreted as the direct or semi-direct impact of anthropogenic sources. In the remaining sites, with a higher degree of isolation from anthropogenic sources, daily cycles present very limited variations both in magnitude and morphology.

The daily variability of O_3 is conditioned by meteorological factors and precursor gases emissions patterns. The concentration peaks are observed in the afternoon following the maximum photochemical activity. The reduction in concentrations during the night is not particularly marked in some sites responding to processes involving air masses, previously loaded with O_3 produced locally or regionally during daytime, which suffer recirculation and generate notable ozone concentrations in remote areas at night (Escudero et al., 2014).

4. Conclusions

This work presents a comprehensive assessment of the levels of atmospheric pollutants in 9 Spanish NP located in the Iberian Peninsula. This has been done working with data (SO_2, NO_x, PM_{10}, $PM_{2.5}$ and O_3) corresponding to the period 2008–2012 obtained from regional background stations belonging to operative monitoring networks. These stations were selected after imposing different criteria in order to guarantee the representativeness with respect to the NP.

The natural and remote characteristics of NP, generally far from major emission sources, and the progressive decline in the use of S-rich fuels result in low SO_2 concentrations in all NP. NO_x levels were low although, in some parks (DON, SNE or PEU), the influence of main traffic pathways and certain cities generate higher concentrations. The seasonal variability of NO_x is characterised by higher winter levels due to greater emissions and reduced photochemical activity which reduces NO_2 photolysis and, as consequence of lower O_3 levels, the destruction of NO by titration. The analysis of daily variability demonstrate the direct influence of traffic and other anthropogenic sources on the 3 NP mentioned above where two concentration peaks associated with traffic emissions in rush hours were observed. At these sites, marked reductions were detected for weekends compared to weekdays confirming the impact of anthropogenic sources.

PM_{10} and $PM_{2.5}$ levels were moderate but, as in the case of NO_x, the sites with a higher presence of anthropogenic sources around them (GUA, SNE, PEU and DON) presented higher concentrations. In SNE and DON the influence of African dust outbreaks can also be a factor for those higher levels. PM variability is marked with higher summer levels due to higher frequency of African events, lower precipitation and increased photochemical production of secondary particles. Moreover, the high vertical extent of the PBL in summer facilitates the arrival of pollutants from urban and industrial areas to NP. A secondary maximum of PM is detected in February–March by the effect of African dust outbreaks and the enhancement of breeze dynamics.

Ozone concentrations are significatively high in NP in Spain. A west-east gradient is associated with climatic differences as the western Iberian Peninsula is more exposed to the Atlantic ventilation than the east. Moreover, the specific orography of the eastern side of the Iberian Peninsula aids to the regional circulation and aging of air masses resulting in elevated O_3. The photochemical origin of O_3 results in a very marked seasonal variability with much higher levels in the spring-summer period.

The conclusions drawn in this work should motivate new research in this field. It is essential to continue collecting data on atmospheric pollutants in NP especially in cases like O_3 due to the elevated levels of this pollutant in background areas and the difficulties for the implementation and evaluation of mitigation plans (Tapia et al., 2016). For this purpose it is basic to use trace level monitors for SO_2 and NO_x and incorporate online PM measurements for describing time evolution. In order to complete the present work focused on long term variability, efforts describing spatial variability or vertical profiles (for example in mountainous regions) of pollutants in each NP should be carried out using dosimetry which is a useful and economically affordable technique. Deposition should be monitored in order to obtain information on incoming fluxes of relevant species such as trace metals or nitrogen. *PM* speciation and source apportionment studies can offer excellent estimation of major atmospheric sources affecting NP. Finally, studies dedicated to evaluate the impact of particular sources (traffic, industrial, agriculture o livestock) in certain NP may be useful to provide a better overview of air quality in these relatively remote but ecologically vulnerable locations.

Acknowledgements

This work was founded by the Fundación Biodiversidad (project AQ-NAT), the CUD (project CUD 2013/18) and the Government of Department of Research, Innovation and University of the Aragón Regional Government and the European Social Found through projects E15 and E75. Air quality data provision is acknowledge to the following entities: MAGRAMA, AEMET, IDAEA-CSIC and the Governments of Aragón, Extremadura, Catalunya, Madrid and Castilla y León. The authors gratefully acknowledge the NOAA-ARL for GDAS data provision and for the use of HYSPLIT4 model. Finally, we would like to thank the two blind reviewers for their useful comments.

References

Adame, J.A., Martínez, M., Sorribas, M., Hidalgo, P.J., Harder, H., Diesch, J.M., Drewnick, F., Song, W., Williams, J., Sinha, V., Hernández-Ceballos, M.A., Vilà-Guerau de Arellano, J., Sander, R., Hosaynali-Beygi, Z., Fischer, H., Lelieveld, J., De la Morena, B., 2014. Meteorology during the domino campaign and its connection with trace gases and aerosols. Atmos. Chem. Phys. 14 (5), 2325–2342.
Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. Science 276 (5315), 1052–1058.
Atkinson, R., 2000. Atmospheric chemistry of {VOCs} and {NOx}. Atmos. Environ. 34 (1214), 2063–2101.
Barberán, A., Henley, J., Fierer, N., Casamayor, E.O., 2014. Structure, inter-annual recurrence, and global-scale connectivity of airborne microbial communities. Sci. Total Environ. 487, 187–195.
Beem, K.B., Raja, S., Schwandner, F.M., Taylor, C., Lee, T., Sullivan, A.P., Carrico, C.M., McMeeking, G.R., Day, D., Levin, E., Hand, J., Kreidenweis, S.M., Schichtel, B., Malm, W.C., Collett, J.L., 2010. Deposition of reactive nitrogen during the Rocky mountain airborne nitrogen and sulfur (RoMANS) study. Environ. Pollut. 158 (3), 862–872.
Benedict, K.B., Chen, X., Sullivan, A.P., Li, Y., Day, D., Prenni, A.J., Levin, E.J.T., Kreidenweis, S.M., Malm, W.C., Schichtel, B.A., Collett, J.L., 2013. Atmospheric concentrations and deposition of reactive nitrogen in Grand Teton National Park. J. Geophys. Res. Atmos. 118 (20), 11875–11887, 2013JD020394.
Burley, J.D., Bytnerowicz, A., Ray, J.D., Schilling, S., Allen, E.B., 2014. Surface ozone in Joshua Tree National Park. Atmos. Environ. 87 (0), 95–107.
Burley, J.D., Ray, J.D., 2007. Surface ozone in Yosemite National Park. Atmos. Environ. 41 (28), 6048–6062.
Burns, D.A., 2003. Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming a review and new analysis of past study results. Atmos. Environ. 37 (7), 921–932.
Camarero, L., Aniz, M., 2010. El sistema de seguimiento de las aguas en el nodo LTER-Aigestortes: tendencias e indicadores de los impactos de la deposicin atmosfrica de N y S. Rev. Ecosistemas 19 (2).
de la Campa, A.S., Pio, C., de la Rosa, J., Querol, X., Alastuey, A., González-Castanedo, Y., 2009. Characterization and origin of {EC} and {OC} particulate matter near the doana national park (sw Spain). Environ. Res. 109 (6), 671–681.
CEAM, 2014. Informe Final Memoria Técnica Proyecto CONOZE- CONtaminación por OZono en España. Technical Report. Fundación Centro de Estudos Ambientales del Mediterráneo.
Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329 (24), 1753–1759. PMID: 8179653.
Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT4 modelling system for trajectories, dispersion, and deposition. Aust. Meteorol. Mag. 47 (4), 295–308.
Eatough, D.J., Du, A., Joseph, J.M., Caka, F.M., Sun, B., Lewis, L., Mangelson, N.F., Eatough, M., Rees, L.B., Eatough, N.L., Farber, R.J., Watson, J.G., 1997. Regional source profiles of sources of SO_x at the Grand Canyon during project MOHAVE. J. Air & Waste Manag. Assoc. 47 (2), 101–118.
EC, 2004. Second Position Paper on Particulate Matter. Technical Report. CAFE Working Group on Particulate Matter, European Comission.
Ellis, R.A., Jacob, D.J., Sulprizio, M.P., Zhang, L., Holmes, C.D., Schichtel, B.A., Blett, T., Porter, E., Pardo, L.H., Lynch, J.A., 2013. Present and future nitrogen deposition to national parks in the United States: critical load exceedances. Atmos. Chem. Phys. 13 (17), 9083–9095.
Engling, G., Herckes, P., Kreidenweis, S.M., Malm, W.C., Collett, J.L., 2006. Composition of the fine organic aerosol in Yosemite National Park during the 2002 Yosemite aerosol characterization study. Atmos. Environ. 40 (16), 2959–2972.
Escudero, M., Castillo, S., Querol, X., Avila, A., Alarcón, M., Viana, M.M., Alastuey, A., Cuevas, E., Rodríguez, S., 2005. Wet and dry african dust episodes over eastern Spain. J. Geophys. Res. Atmos. 110 (D18), D18S08.
Escudero, M., Lozano, A., Hierro, J., del Valle, J., Mantilla, E., 2014. Urban influence on increasing ozone concentrations in a characteristic Mediterranean agglomeration. Atmos. Environ. 99 (0), 322–332.
Escudero, M., Querol, X., Ávila, A., Cuevas, E., 2007. Origin of the exceedances of the European daily {PM} limit value in regional background areas of Spain. Atmos. Environ. 41 (4), 730–744.
Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., Neitlich, P., 2003. Ecological effects of nitrogen deposition in the Western United States. BioScience 53 (4), 404–420.
García-Gómez, H., Garrido, J., Vivanco, M., Lassaletta, L., Rábago, I., Avila, A., Tsyro, S., Sánchez, G., Ortiz, A.G., González-Fernández, I., Alonso, R., 2014. Nitrogen deposition in Spain: modeled patterns and threatened habitats within the Natura 2000 network. Sci. Total Environ. 485486 (0), 450–460.
González-Castanedo, Y., Sánchez-Rodas, D., de la Campa, A.S., Pandolfi, M., Alastuey, A., Cachorro, V., Querol, X., de la Rosa, J., 2015. Arsenic species in atmospheric particulate matter as tracer of the air quality of doana natural park (sw Spain). Chemosphere 119, 1296–1303.
Hafner, W., Solorzano, N., Jaffe, D., 2007. Analysis of rainfall and fine aerosol data using clustered trajectory analysis for National Park sites in the Western {US}. Atmos. Environ. 41 (14), 3071–3081.
Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J., Buchmann, B., 2010. Assessment of parameters describing representativeness of air quality in-situ measurement sites. Atmos. Chem. Phys. 10 (8), 3561–3581.
IPCC, Climate Change, 2013. The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University press, 2013.
Irwin, J.G., Campbell, G., Vincent, K., 2002. Trends in sulphate and nitrate wet deposition over the United Kingdom: 19861999. Atmos. Environ. 36 (17), 2867–2879.
Janssen, S., Dumont, G., Fierens, F., Deutsch, F., Maiheu, B., Celis, D., Trimpeneers, E., Mensink, C., 2012. Land use to characterize spatial representativeness of air quality monitoring stations and its relevance for model validation. Atmos. Environ. 59, 492–500.
Kucera, V., Fitz, S., 1995. Direct and indirect air pollution effects on materials including cultural monuments. Water, Air, Soil Pollut. 85 (1), 153–165.
Larssen, S., Sluyter, R., Helmis, C., 1999. Criteria for EUROAIRNET. The EEA Air Quality Monitoring and Information Network. Technical Report. EEA.
de Leeuw, F.A., 2000. Trends in ground level ozone concentrations in the European Union. Environ. Sci. Policy 3 (4), 189–199.
Malm, W.C., Day, D.E., Carrico, C., Kreidenweis, S.M., Collett, J.L., McMeeking, G., Lee, T., Carrillo, J., Schichtel, B., 2005. Intercomparison and closure calculations using measurements of aerosol species and optical properties during the Yosemite aerosol characterization study. J. Geophys. Res. Atmos. 110 (D14), D14302.
McMeeking, G.R., Kreidenweis, S.M., Carrico, C.M., Collett, J.L., Day, D.E., Malm, W.C., 2005. Observations of smoke-influenced aerosol during the Yosemite aerosol characterization study: 2. Aerosol Scatt. absorbing Prop. J. Geophys. Res. Atmos. 110 (D18), D18209.
Millán, M., Salvador, R., Mantilla, E., Nano, B.A., 1996. Meteorology and photochemical air pollution in Southern Europe: experimental results from {EC} research projects. Atmos. Environ. 30 (12), 1909–1924.
Pandolfi, M., Tobias, A., Alastuey, A., Sunyer, J., Schwartz, J., Lorente, J., Pey, J., Querol, X., 2014. Effect of atmospheric mixing layer depth variations on urban air quality and daily mortality during Saharan dust outbreaks. Sci. Total Environ. 494495, 283–289.
Paoletti, E., 2006. Impact of ozone on Mediterranean forests: a review. Environ. Pollut. 144 (2), 463–474.
Percy, K., Karnosky, D., 2007. Air quality in natural areas: interface between the public, science and regulation. Environ. Pollut. 149 (3), 256–267 (Air Pollution and Vegetation Effects Research in National Parks and Natural Areas: Implications for Science, Policy and Management).
Pey, J., Pérez, N., Querol, X., Alastuey, A., Cusack, M., Reche, C., 2010. Intense winter atmospheric pollution episodes affecting the western mediterranean. Sci. Total Environ. 408 (8), 1951–1959.
Pey, J., Querol, X., Alastuey, A., Forastiere, F., Stafoggia, M., 2013. African dust outbreaks over the mediterranean basin during 2001-2011: Pm_{10} concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology. Atmos. Chem. Phys. 13 (3), 1395–1410.
Pitchford, M., Green, M., Kuhns, H., Farber, R.J., 2000. Characterization of regional transport and dispersion using project MOHAVE tracer data. J. Air & Waste Manag. Assoc. 50 (5), 733–745.
Preisler, H.K., Zhong, S.S., Esperanza, A., Brown, T.J., Bytnerowicz, A., Tarnay, L., 2010. Estimating contribution of wildland fires to ambient ozone levels in National Parks in the Sierra Nevada, California. Environ. Pollut. 158 (3), 778–787.
Prenni, A., Levin, E., Benedict, K., Sullivan, A., Schurman, M., Gebhart, K., Day, D.,

Carrico, C., Malm, W., Schichtel Jr., B., J.C., Kreidenweis, S., 2014. Gas-phase reactive nitrogen near Grand Teton national park: impacts of transport, anthropogenic emissions, and biomass burning. Atmos. Environ. 89 (0), 749–756.
Querol, X., Alastuey, A., Pandolfi, M., Reche, C., Pérez, N., Minguillón, M., Moreno, T., Viana, M., Escudero, M., Orío, A., Pallarés, M., Reina, F., 2014. 20012012 trends on air quality in Spain. Sci. Total Environ. 490 (0), 957–969.
Ray, J.D., 2001. Spatial distribution of tropospheric ozone in national parks of California: interpretation of passive-sampler data. TheScientificWorldJOURNAL 1 (0), 483–497.
Rodríguez, S., Querol, X., Alastuey, A., Mantilla, E., 2002. Origin of high summer {PM10} and {TSP} concentrations at rural sites in eastern Spain. Atmos. Environ. 36 (19), 3101–3112.
Sanz, M., Sanz, F., Calatayud, V., Na, G.S.P., 2007. Ozone in Spain's national parks and protected forests. TheScientificWorldJOURNAL 7 (0), 67–77.
Screpanti, A., Marco, A.D., 2009. Corrosion on cultural heritage buildings in Italy: a role for ozone? Environ. Pollut. 157 (5), 1513–1520 (Special Issue Section: Ozone and Mediterranean Ecology: Plants, People, Problems).
Seidel, D., Zhang, Y., Beljaars, A., Golaz, J.C., Jacobson, A., Medeiros, B., 2012. Climatology of the planetary boundary layer over the continental United States and europe. J. Geophys. Res. Atmos. 117 (D17), D17106.
Sicard, P., De Marco, A., Troussier, F., Renou, C., Vas, N., Paoletti, E., 2013. Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities. Atmos. Environ. 79, 705–715.
Tapia, O., Escudero, M., Lozano, Anzano, J., Mantilla, E., 2016. New classification scheme for ozone monitoring stations based on frequency distribution of hourly data. Sci. Total Environ. 544, 1–9.
Temple, P.J., 1989. Oxidant air pollution effects on plants of joshua tree national monument. Environ. Pollut. 57 (1), 35–47.
Troen, I., Mahrt, L., 1986. A simple model of the atmospheric boundary layer; sensitivity to surface evaporation. Bound. Layer. Meteorol. 37, 129–148.
UNECE, 1988. Final Draft Report of ECE Critical Levels Workshop. United Nations Economic Commission for Europe. Technical Report.
Villanueva, F., Tapia, A., Notario, A., Albaladejo, J., Martínez, E., 2014. Ambient levels and temporal trends of voc_s, including carbonyl compounds, and ozone at Cabañeros national park border. Spain. Atmos. Environ. 85 (0), 256–265.
WHO, 2006. Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide: Global Update 2005. WHO Regional Office for Europe, Copenhagen, Denmark.
WHO, 2008. Health Risks of Ozone from Long-range Transboundary Air Pollution. WHO Regional Office for Europe, Copenhagen, Denmark.
Zhang, Y., Gao, Z., Li, D., Li, Y., Zhang, N., Zhao, X., Chen, J., 2014. On the computation of planetary boundary-layer height using the bulk richardson number method. Geosci. Model Dev. 7, 2599–2611.