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Trends of particulate matter ($PM_{2.5}$) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)

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Abstract

The time variability and long term trends of $PM_{2.5}$ (particulate matter of diameter <2.5 µm) at various regional background (RB) sites across Europe are studied and interpreted in this work. Long-term trends of $PM_{2.5}$ concentrations are relatively scarce across Europe, with few studies outlining the changes measured in $PM_{2.5}$ concentrations over a significant period of time. To this end, data on mean annual levels of $PM_{2.5}$ measured at Montseny (MSY, North East Spain) and various RB sites in Spain and Europe are evaluated and compared, and subsequently analysed for statistically significant trends. The MSY site registered higher average $PM_{2.5}$ levels than those measured at a selection of other RB sites across Spain, Portugal, Germany and Scandinavia, but lower than those measured in Switzerland, Italy and Austria.

Reductions in $PM_{2.5}$ were observed across all stations in Spain and Europe to varying degrees. MSY underwent a statistically significant reduction since measurements began, indicating a year-on-year gradual decrease ($-3.7\,\mu g\,m^{-3}$, calculated from the final year of data compared to the mean). Similar trends were observed in other RB sites across Spain ($-1.9\,\mu g\,m^{-3}$). Reductions recorded in $PM_{2.5}$ across Europe were varied, with many experiencing gradual, year-on-year decreases ($-1.8\,\mu g\,m^{-3}$). These reductions have been attributed to various causes: the introduction and implementation of pollution abatement strategies in EU member states, the effect of the current economic crisis on emissions of $PM_{2.5}$ and the influence of anomalous meteorology observed during the winters of 2009 and 2010. The North Atlantic Oscillation (NAO), a large scale meteorological phenomenon most prevalent during winter, was observed to influence the frequency of Saharan dust intrusions across the Iberian Peninsula.

Chemical composition of $PM_{2.5}$ at MSY is characterised by high levels of organic matter (OM) and sulphate, followed by crustal material, nitrate and ammonia. Sea Spray and finally elemental carbon (EC) comprised a minor part of the total $PM_{2.5}$ mass. Statistical trend analysis was performed on the various chemical components of $PM_{2.5}$ recorded at MSY to determine which components were accountable for the decrease in

$PM_{2.5}$ concentration. It is shown that OM underwent the largest decrease over the time period with a statistically significant trend ($-1.3\,\mu g\,m^{-3}$ of the mean), followed by sulphate ($-0.8\,\mu g\,m^{-3}$), ammonium ($-0.5\,\mu g\,m^{-3}$) and nitrate ($-0.4\,\mu g\,m^{-3}$). Conversely, sea spray, EC and crustal material reductions were found to be negligible.

1 Introduction

One of the greatest challenges facing the global environment is the presence of tropospheric aerosols, both natural and anthropogenic, and their impact on health (Pope and Dockery, 2006), the Earth's climate (IPCC, 2007), visibility, ecosystems and building materials. For these reasons, emissions and ambient levels of atmospheric pollutants are currently regulated through various European Commission (EC) directives. The directive 2008/50/EC establishes limit and target values for ambient air $PM_{2.5}$ in all member states of the European Union (EU). Even though these target values for $PM_{2.5}$ did not come into force until 2010 (with limit values being enforced in 2015 followed by an obligatory reduction of a variable percentage of average $PM_{2.5}$ levels by 2018–2020 in each country, calculated as a fraction of the mean $PM_{2.5}$ levels during 2008–2010), levels of $PM_{2.5}$ have been decreasing throughout Europe for a number of years, as outlined in this paper. Thus, it can be reasonably assumed that this Europe wide reduction is a result of the implementation of emission abatement strategies enforced in the EU and the introduction of the Integrated Pollution Prevention and Control (IPPC) directive. The abatement strategies, until recently, have mostly been concerned with gaseous emissions and PM_{10}, but cleaner industrial practices and reduced traffic emissions would naturally have a subsidiary effect on other major pollutants, $PM_{2.5}$ included. Previous studies have observed a decreasing trend for $PM_{2.5}$ for many countries in Europe, as outlined in the EMEP report 4/2011 (Tsyro et al., 2011). In fact, the findings in the report show that almost all countries in Western Europe with long term $PM_{2.5}$ measurements have undergone some reduction to varying degrees since 2000. Furthermore, a recent article published described PM variability in various urban and

rural sites in Europe, and indicated that PM_{10} and $PM_{2.5}$ have reduced considerably over the past decade (Barmpadimos et al., 2012).

However, other factors appear to have some influence on PM concentrations observed. Since mid-2008, Europe and much of the Western world has been in the grips of a severe economic recession which, at the time of writing this article, appears to show no sign of abating. Indeed, this economic crisis has been most severely felt in the peripheral economic states of Europe such as Spain and Portugal, and Europe's fourth largest economy, Italy. A study performed by Arruti et al. (2011) has observed a direct link between levels of industrial trace elements and some economic indicators in northern Spain from 2008–2009. However, the study did not discover any direct relationship between the economic downturn and ambient PM levels. Anthropogenic activities have long been associated with air pollution, through fuel oil combustion, industrial activities, traffic emissions and construction, to name a few. The economic recession has severely impacted these activities, and the possible resulting effect is a net reduction in pollution.

Finally, unusual meteorology has possibly played a significant role in the changes in PM observed in the last two years. Millán et al. (1997), Soriano et al. (2001), Gangoiti et al. (2001), Rodríguez et al. (2002, 2003), Jorba et al. (2004) and Pérez et al. (2004), among others, have all described the relationship between air quality in the Western Mediterranean Basin (WMB) and the effect of mesoscale and local meteorological processes. However, meteorology on a much larger scale also plays an important role on influencing annual PM levels. In the Northern Hemisphere, one of the most consistent and prominent large-scale patterns of atmospheric variability is the North Atlantic Oscillation (NAO), especially during the winter months. Fluctuations between positive and negative phases of NAO (calculated from the pressure differences between the Icelandic low pressure and Azores high pressure systems) can produce large changes in wind speed, temperature and precipitation across Europe (Hurrell et al., 2003). The winters of 2009 and 2010 were characterised by intensely negative NAO index (NAOi) and extreme cold spells for much of Northern Europe. Vicente-Serrano et al. (2011)

linked the intense negative phase of NAO to the extreme rainfall recorded in the Iberian Peninsula for the same period; higher precipitation would undoubtedly affect the levels of PM on a regional scale. Further studies have shown the effect of NAO on the transport of North African Dust (Moulin et al., 1997). The influence of North African dust outbreaks on PM in NE Spain is very significant (Querol et al., 1998a, b); the inhibition of Saharan dust reaching this area of the Iberian Peninsula would have an overall reducing effect on total PM levels.

The Montseny (MSY) monitoring station forms an important part of a Europe-wide measurement network EUSAAR (European Supersites for Atmospheric Aerosol Research), which aims to integrate and homogenise the monitoring of similar atmospheric aerosol properties performed by 21 stations across Europe. The MSY station provides important information on regional background (RB) aerosols in the Western Mediterranean Basin (WMB). The Spanish coastline, especially in the NE towards the border with France, is densely populated and highly industrialised. Measurements of aerosols performed at RB sites such as MSY, relatively distant from the influence of specific emissions sources, provide more accurate data on long-term trends of aerosols. A number of studies have outlined the variability of PM at MSY and the complex atmospheric dynamics that occur there (Querol et al., 2009; Pérez et al., 2008; Pey et al., 2010). The variability of levels and PM chemical composition from 2002–2007 at MSY has been well documented by Pey et al. (2009). This present work investigates the trends observed through the extension of the data time series (2002–2010), allowing for greater insight into the PM inter-annual trends occurring. The $PM_{2.5}$ trends for many stations across Europe, and to a greater extent Spain, are analysed and compared to those of MSY. These trends are analysed for statistical significance, in order to determine if the decreases observed are gradual and uniform. Special focus is then given to the in-depth investigation into the temporal trends observed, not only for $PM_{2.5}$, but also to the various chemical components of $PM_{2.5}$ at MSY.

2 Methodology

Table 1 lists the various stations (and corresponding countries) used in this study for comparison of $PM_{2.5}$ levels. The Montseny station (MSY) is located in the Montseny natural park 40 km to the NNE of the Barcelona urban area, and 25 km from the Mediterranean coast. The station is located on the upper walls of a valley extending perpendicularly from the Catalan Pre-Coastal ranges, in a densely forested area known as La Castanya. The station is situated relatively far from urban and industrial zones, but the region is generally densely populated and heavily industrialised, and local anthropogenic emissions can affect this site under specific meteorological conditions. Atmospheric dynamics and aerosol variability at MSY has been described in detail by Pérez at al. (2008).

Samples of $PM_{2.5}$ were collected on quartz fibre filters (Schleicher and Schuell, QF20 until 2009, Munktell thereafter) for 24 h periods roughly once a week until 2007, and consecutively every four days from 2008, with high volume samplers ($30\,m^3\,h^{-1}$) DIGITEL-DH80 and MCV-CAV, equipped with a $PM_{2.5}$ cut off inlet (manufactured by DIGITEL). Filters were treated prior to sampling by pre-heating at 200 °C for 4 h, conditioned at 20–25 °C and 25–30 % relative humidity for at least 24 h, and weighed three times on three consecutive days. Sampling began in March 2002 and 403 samples of $PM_{2.5}$ were taken and chemically analysed from 22/03/2002 to 31 December 2010. PM mass concentrations were determined by standard gravimetric procedures (see Querol et al., 2001).

Filters were analysed using different instrumental analysis techniques to determine concentrations of a range of elements and components, as described by Querol et al. (2008). After weighing, 1/2 of each filter was acid digested ($HF:HNO_3:HClO_4$) for the determination of major and trace elements. Major component (Al, Ca, Na, Mg, Fe, K) concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy, ICP-AES (IRIS Advantage TJA solutions, THERMO). Trace element concentrations were determined by means of Inductively Coupled Plasma Mass Spec-

troscopy, ICP-MS (X Series II, THERMO). Water soluble ions SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- were determined from water leachates from 1/4 of the filter and analysed by Ion Chromatography HPLC (High Performance Liquid Chromatography) using a WATERS IC-pakTM anion column and WATERS 432 conductivity detector. NH_4^+ was determined by an ion specific electrode. The remaining 1/4 of each filter was used for the elemental analysis of Organic and Elemental Carbon (OC and EC) by a thermal-optical transmission technique using a Sunset Laboratory OCEC Analyser. Organic Matter (OM) is calculated from OC by multiplying by a factor of 2.1 as suggested by Turpin et al. (2001) and Aiken et al. (2005). SiO_2 and CO_3^{2-} were indirectly determined from empirical formulas (Querol et al., 2001). These combined procedures allowed for the determination of concentrations of major components (OC, EC, SiO_2, CO_2^{3-}, Al, Ca, Na, Mg, Fe, K, NO_3^-, SO_4^{2-}, NH_4^+ and Cl^-) and trace elements (Li, P, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Pb, among others). The combined sum of the aforementioned components accounted for 75–85 % of the total PM mass.

Stations in Spain from which data is used in this study (Cabo de Creus, Els Torms, Zarra, Viznar, Barcarrota, O Saviñao, Niembro, Campisábalos, Peñausende and Risco Llano) are all members of EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe). Measurements were performed gravimetrically on a daily basis using EN UNE 14907 high volume samplers (MCV PM1025) in accordance with standard procedures outlined by European Air Quality Directive 2008/50/CE and the EMEP EN 14907:2005 standard. Of the remaining European sites, all measurements were determined gravimetrically on a daily basis except the following stations: Pfälzerwald-Hortenkopf, Virolahti, Utö, Fundão, Chamusca, Lamas de Olo and Ervedeira performed measurements by Beta Ray Attenuation providing hourly averages of $PM_{2.5}$. Measurements at Vavihill and Aspvreten were performed by TEOM with hourly resolution. Measurements at Hyytiälä were recorded on a daily basis using an impactor. Ispra employed a filter pack and measurements were performed on a daily basis. Finally, a Sierra Dichotomous Sampler was employed at Birkenes providing $PM_{2.5}$ measurements at a weekly resolution.

All $PM_{2.5}$ data and details of the operational status and site characteristics of the stations can be found on the EMEP website (www.emep.int) and the AIRBASE website (http://acm.eionet.europa.eu/databases/airbase/).

Temporal trend analysis was performed for all the stations where sufficient data was available (see Table 2 for the list of stations) by means of the nonparametric Mann-Kendall test for the trend and the nonparametric Sen's method for the magnitude of the trend. The MAKESENS (**Ma**nn-**Ke**ndall test for trend and **Sen's** slope estimate) template application was employed (Salmi et al., 2002). The Mann-Kendall test is applicable for the detection of a monotonic increasing or decreasing trend of a time series and the Sen's method estimates the slope of the linear trend (Gilbert 1987). Thus, analysis was applied to the mean annual and monthly concentrations of $PM_{2.5}$ and its various chemical components. The significance of the trend is symbolised as (α) and the level of significance is weighted from most significant to the least significant as: ($\alpha = 0.001 > 0.01 > 0.05 > 0.1$).

3 Results and discussion

3.1 Mean $PM_{2.5}$ levels

Mean $PM_{2.5}$ levels recorded at MSY (determined gravimetrically) from 2002 to 2010 were 12.6 $\mu g\,m^{-3}$. $PM_{2.5}$ levels were elevated when compared with Spanish EMEP stations (Table 1). The average $PM_{2.5}$ concentration for 10 EMEP RB sites across the Iberian Peninsula (IP) for the same time period was 8.6 $\mu g\,m^{-3}$, and the average value for two other RB stations in the NE IP (namely Els Torms and Cabo de Creus) was 10.5 $\mu g\,m^{-3}$. Thus, the MSY station registered higher levels of PM compared to average concentrations across Spain (+38 % difference with respect to the mean) and those registered from stations in the NE of Spain (+17 %). This surplus may be attributed to anthropogenic influences. The greater area surrounding MSY, especially the valleys

in the pre-coastal depression, is densely populated and highly industrialised, being a significant source of pollution reaching the MSY site.

Comparing these values with other RB sites across Europe (Table 1), concentrations measured at MSY were considerably higher (+37 %) than those in Portugal (9.4 $\mu g\,m^{-3}$), Germany (10 $\mu g\,m^{-3}$) and Scandinavia (6.6 $\mu g\,m^{-3}$). They were slightly lower than levels recorded in Switzerland (14.5 $\mu g\,m^{-3}$) and significantly lower than levels recorded in Austria (19.7 $\mu g\,m^{-3}$). Ispra recorded the highest levels of all the stations included in this work, with $PM_{2.5}$ of 26.2 $\mu g\,m^{-3}$.

3.2 Interannual trends across Spain and Europe

A decreasing trend for $PM_{2.5}$ has been observed in MSY since measurements began in 2002 (Fig. 1). Furthermore, this decreasing trend has been observed not only across Spain, but throughout Europe (Fig. 2). Of the stations listed in Table 1, statistical trend analysis using the Mann Kendall test was performed where 9 valid data points were available, with results shown in Table 2. What was immediately apparent was that levels of $PM_{2.5}$ in all stations have decreased to some extent. However, not all have undergone a uniform reduction, with some having a statistically relevant trend (significance level $\alpha > 0.1$), where others have decreased in the absence of a statistically significant trend, in which case α is not shown. The three stations from the NE Iberian peninsula i.e. MSY, Els Torms and Cabo de Creus, have experienced reductions of 35 %, 40 % and 49 % with $\alpha = 0.01$, 0.05 and 0.001 respectively. Peñausende has also experienced a significant decrease ($\alpha = 0.001$) of 42 % since 2002.

On average, for the RB stations used in this study a reduction of 32 % has been observed in $PM_{2.5}$ levels since 2002 throughout Spain, 31 % at Illmitz, 36 % at Payerne, 34 % at Ispra, 35 % in Sweden, 32 % across Germany, 32 % in Finland, 41 % in Norway and 38 % in Portugal. There were only two stations, Niembro in the north and Viznar in southern Spain, which registered low decreases of only 7 % and 14 % respectively. The proximity of Viznar in southern Spain to the urbanised area of Granada (20 km) places it under greater influence of urban emissions, which may account for the comparatively

smaller decrease of 14 % in $PM_{2.5}$. The close proximity of Viznar to North Africa also exposes the site to more frequent Saharan dust intrusions. However a 14 % reduction in $PM_{2.5}$, in the context of a RB site with some urban influence, is still quite significant. Niembro is a low altitude coastal site on the Atlantic coast. The station is also located in close proximity to a densely industrialised area power generation plants which may be an important source of PM emitted locally, accounting for this lower reduction observed. Stations located in the central IP i.e. Risco Llano, Campisábalos and Peñausende all registered very low concentrations of $PM_{2.5}$ (Table 1). A statistically significant decreasing trend was not observed for Risco Llano, unlike that observed for Campisábalos and Peñausende, but $PM_{2.5}$ levels have decreased nonetheless.

Thus, excluding Viznar and Niembro, the percentage reduction observed across Spain and Europe ranges from a minimum of 20 % (Risco Llano) to a maximum of 49 % (Cabo de Creus). What is most striking is that these decreases are so similar across Europe, the median percentage reduction being 35 %.

However, even though all the reductions may not be statistically relevant (either due to the fact that less than 9 years measurement data is available, or that the reduction has not been uniform), the decrease in $PM_{2.5}$ appears to be most dramatic in all measurement stations in the IP and Ispra in Italy from 2008 onwards, as can be seen in Figs. 1 and 2.

As illustrated in Fig. 1 a marked decrease was observed for each area of Spain in 2008 (highlighted in grey). Stations are categorised according to their location in Spain and values are mean $PM_{2.5}$ concentrations of the stations for that location for each year: Niembro and O Saviñao are categorised as North; Viznar and Barcarrota are South; Peñausende, Campisábolos and Risco Llano are considered Central; Zarra is East; Cabo de Creus and Els Torms are North East. Levels reached a minimum in 2008, followed by a slight increase in 2009 (for all except central Spain), and a reduction once again in 2010. MSY followed a similar trend to that observed for the other stations in the NE peninsula, albeit with slightly higher levels measured in comparison. The fact that the PM levels here follow a similar trend verifies that the trend is real and observed

across the region. In fact, this decreasing trend is observed for many stations across Europe (Fig. 2).

For some stations in Germany, Austria, Switzerland, Finland and Sweden, levels of $PM_{2.5}$ experienced noticeable decreases from 2007 onwards. For example, in Vavihill, Sweden and Waldhof in Germany, a sharp decrease was recorded of 4 $\mu g\,m^{-3}$ and 5 $\mu g\,m^{-3}$ between 2006 and 2007, respectively (Fig. 2). A similar reduction, although not quite as pronounced, was observed for stations Illmitz, Payerne, Utö, Aspverten, Virolahti, Schwartenberg and Schauinsland. This gradual reduction observed across Europe is possibly a direct result of the implementation of the aforementioned pollution abatement strategies. Indeed, the countries in which these stations are located have to a large extent avoided economic recession compared to the peripheral European states such as Spain, Portugal and Italy. Thus, reductions there have not been quite as pronounced as those recorded for the last two years in the IP and Ispra, but exist nonetheless.

Stations in Portugal and Italy displayed similar reductions as those observed in Spain (Fig. 2). The sharpest reductions were observed between 2007 and 2008 (as compared to levels in most of the other European stations which generally dropped gradually). Levels measured in Lamas de Olo dropped 6.8 $\mu g\,m^{-3}$ during 2007-2008 from 10.8 to 3.9 $\mu g\,m^{-3}$ (Fig. 2). Decreases in Fundão and Chamusca were more gradual from 2007–2009, decreasing by 2.6 $\mu g\,m^{-3}$ and 3.4 $\mu g\,m^{-3}$, respectively. This suggests that similar processes are influencing PM levels not only in Spain, but across the IP including Portugal. The reduction observed at Ispra in northern Italy was also most pronounced from 2008 onwards. Although levels do exhibit a decreasing trend across the time series, especially since 2005, a large drop in $PM_{2.5}$ was observed between 2007 (26 $\mu g\,m^{-3}$) and 2008 (20 $\mu g\,m^{-3}$). This observed decrease from 2008 onwards indicates that these stations in Spain, Portugal and Italy, although geographically distant, share some factor in common causing background levels of $PM_{2.5}$ to decrease all within the same time frame. A reduction in emissions of pollutants as a result of the downturn in the economy may possibly be this factor. A recent study by Barmpadimos

et al. (2012) also observed a decreasing trend in PM_{10} and $PM_{2.5}$ in various urban and rural background sites in Europe, some of which are also included in this study (namely, Illmitz, Waldhof, Payerne and Peñausende). The article concluded that PM_{10} and $PM_{2.5}$ have reduced considerably over the past ten years due to non-meteorological factors. Indeed, for the station at Peñausende, the authors concluded that a decrease in anthropogenic emissions was likely to be accountable for the reduction observed in $PM_{2.5}$ rather than meteorology.

3.3 PM speciation

As shown in Fig. 3 the main chemical components of $PM_{2.5}$ (12.6 $\mu g\,m^{-3}$) at MSY are organic matter (OM; 4.2 $\mu g\,m^{-3}$; 33 %), SO_4^{2-} (2.4 $\mu g\,m^{-3}$; 19 %), crustal material (1.1 $\mu g\,m^{-3}$; 9 %), NO_3^- (1.0 $\mu g\,m^{-3}$; 8 %), NH_4^+ (1.0 $\mu g\,m^{-3}$; 8 %), sea spray (0.3 $\mu g\,m^{-3}$; 2 %) and finally elemental carbon (EC; 0.2 $\mu g\,m^{-3}$; 2 %). The unaccounted mass is 19 % of the total PM mass and is attributed to water retention on the filters.

In relative proportions, OM was by far the major component of $PM_{2.5}$ at MSY. Sources of OM at MSY are varied, and can be attributed to secondary organic aerosol (SOA) formed after the emissions of anthropogenic volatile organic compounds (VOCs) from industry, road traffic, biomass burning emissions and also biogenic VOCs (Peñuelas et al., 1999). Sulphate was the second most abundant compound measured at MSY and is associated with industrial, shipping and power generation emissions. Nitrate and ammonium levels recorded at MSY were similar at 8 % for both. Owing to the thermal instability of ammonium nitrate, the most common compound of nitrate at this site, the majority of nitrate was measured during the winter months. During summer months, when ammonium nitrate is volatilised, ammonium concentrations measured were typically in the sulphate form. Crustal material registered in $PM_{2.5}$ 9 % of the total mass. The majority of crustal material at MSY is typically found in the coarse fraction ($PM_{2.5-10}$) and does not influence levels of $PM_{2.5}$ to a great extent, but Saharan dust intrusions can influence the crustal load measured in $PM_{2.5}$ (Pey et al., 2009). Levels

of elemental carbon (EC) comprised only 2 % of the total mass. EC emissions are associated with fuel-oil combustion and biomass burning emissions. Biomass burning, both anthropogenic and natural, could possibly be a significant source of EC at MSY, as it is a rural forested site with agricultural land nearby.

3.4 Inter-annual trends at MSY for $PM_{2.5}$ and chemical composition

The analysis of inter-annual trends of $PM_{2.5}$ levels measured at MSY, and the respective trend analysis of its chemical components, has revealed possible explanations for the reduction observed over the past 9 yr, and may possibly provide insight into the reduction observed across Europe.

3.4.1 $PM_{2.5}$ trends

Temporal trend analyses were applied to the annual and seasonal chemistry data sets from MSY from 2002 to 2010. The Mann-Kendall tests showed significant temporal trends for the total mass of $PM_{2.5}$ ($\alpha = 0.01$) with a 35 % decrease observed over the total measurement time period (Fig. 4), the equivalent of 6 $\mu g\,m^{-3}$ of $PM_{2.5}$. On a seasonal basis, winter was the only season that registered a statistically significant year-on-year decreasing trend ($\alpha = 0.05$), with a decrease of 35 %. MSY is regularly affected by intense anthropogenic pollution episodes that occur during the colder months i.e. from October to March. The occurrence of these polluted winter anticyclonic episodes (WAE), their intensity and their affect on pollution levels, has been outlined by Pey et al. (2010). The combination of various factors may account for this reduction that occurred only in the winter season; a reduction in anthropogenic emissions due to pollution abatement strategies, the economic recession and quite possibly the unusual meteorology that has occurred during winter for the last few years. The North Atlantic Oscillation (NAO) is a large-scale meridional oscillation in atmospheric mass, with centres of action near Iceland and over the subtropical Atlantic (Visbeck et al., 2001). It is one of the leading climate modes in the North Atlantic region (Hurrell et al., 2003),

and influences climate variability, e.g. temperature, precipitation and wind, especially during the winter (Hurrell and Deser, 2009). When the pressure gradient between the Icelandic low and the subtropical high pressure centre during winter is more intense than normal (positive NAO), the westerly winds are stronger across northern Europe, bringing Atlantic air masses over the continent, associated with mild temperatures and higher precipitation, and dryer conditions across southern Europe. When this pressure gradient is low (negative NAO), cold and dry air masses often dominate over northern Europe, and the Atlantic weather systems and storm tracks tend toward a more southerly trajectory, bringing higher than normal precipitation levels across the Iberian peninsula (Vicente-Serrano et al., 2011), as occurred during winter 2009 and 2010. Indeed, winter 2010 was notable for two reasons; unusually high precipitation over the IP which coincided with one of the most negative NAOi since measurements began (reported in Vincente-Serrano et al. (2011) as the end of the 19th century or beginning of the 20th century), and one of the coldest winters in decades across northern Europe. Incidentally, winter 2010 also registered the lowest PM levels recorded at MSY since 2002. The cleaning effect of Atlantic Advection on MSY is significant and such episodes are associated with low PM events (Pérez et al., 2008). Thus, due to the enhanced Atlantic Advection (as a result of the negative NAO), PM levels were observed to be considerably lower compared to other winters. As mentioned previously, the occurrence of Saharan dust intrusions over the IP can affect PM levels significantly. Fig. 5 displays the linear relationship observed between the frequency of NAF episodes (in days) and the corresponding NAO index for the winter months Dec, Jan, Feb and March. It can be seen that for winters with positive (negative) NAO indices, NAF episodes were more (less) frequent. This suggests that when NAO is more intensely positive, the probability of air masses from North Africa reaching the IP is much higher. Conversely, when NAO is negative, intense Atlantic Advection directed over the IP can act as a blocker to North African air masses and prevent these air masses moving northward. This influence is most felt in the north of the IP i.e. closer to the Atlantic Ocean, and the intensity weakens with greater distance from the Atlantic Ocean. However, for all parts of the

peninsula, if the NAO index is sufficiently positive or negative, its effects are felt across the country. This theory agrees with that proposed by Moulin et al. (1997).

3.4.2 Organic and Elemental Carbon

Figure 4 shows the temporal trends for OC and EC concentrations recorded from 2002 to 2010 by means of the Mann-Kendall test and Sen's method using MAKESENS. OC exhibited a decreasing trend since 2002 with very high statistical significance (α=0.001), and a reduction of 48 % over the total measurement period. This reduction is the equivalent of 1.6 $\mu g\,m^{-3}$ of OC from a maximum in 2004 of 2.9 $\mu g\,m^{-3}$ to a minimum of 1.3 $\mu g\,m^{-3}$ in 2010. This decreasing trend was observed across all seasons, with varying levels of significance (spring (α = 0.01), summer (α=0.01), autumn (α=0.05), winter (α = 0.05)), verifying that the reduction was real, but also seasonally dependent. Figure 6 shows the time evolution of a selection of components of $PM_{2.5}$, including OC. OC followed a clear seasonal trend, with maximum concentrations registered in summer coinciding with the lowest renewal of the atmosphere at a regional scale (Rodríguez et al., 2002; Pérez et al., 2008) and higher biogenic emissions of VOCs (Seco et al., 2011). Secondary peaks in concentration also occurred during WAE, followed by sharp reductions in spring due to higher precipitation and Atlantic Advection episodes. The intensity of the seasonal cycles clearly began to diminish from 2007 onwards. The reduction observed in OC is most probably a result of a reduction of OC emissions or precursors from anthropogenic sources, as natural emissions of OC would not be expected to decrease. Previous studies at MSY have shown that the fraction of OC in PM_1 that is mainly attributed to road traffic accounts for 31 % of total OC in winter and 25 % in summer (Minguillon et al., 2011). Measurements of known tracers for biomass burning emissions, such as K^+, would be useful to help determine the contribution of biomass burning to levels of OC at MSY. As stated previously, OM (calculated from measured OC) accounted for 44 % of total $PM_{2.5}$. Thus, much of the reduction observed for $PM_{2.5}$ can partly be attributed to the reduction in OC.

EC levels have not shown any statistically significant trend since measurements began, and levels did not vary very much on a yearly basis (0.15–0.25 $\mu g\,m^{-3}$). A minimum value was recorded in 2006 (0.15 $\mu g\,m^{-3}$) and a maximum value was recorded in 2004 and 2008 (0.25 $\mu g\,m^{-3}$). The difference between the maximum and minimum concentrations was not very large. On a seasonal basis, there is an indication that EC levels have actually shown an increasing trend since 2008, especially in winter and autumn. This is contrary to what has been observed for many other anthropogenic pollutants at MSY, but EC may be closely related to local domestic and agricultural biomass burning emissions.

3.4.3 Secondary Inorganic Aerosols

A significant reduction has also been observed for the Secondary Inorganic Aerosols (SIAs) at MSY, including sulphate, nitrate, and ammonium. As stated previously, SIAs comprised 44 % of the total sum of the chemical components of $PM_{2.5}$, thus it stands to reason that a reduction for each SIA would have an overall reducing effect on the total $PM_{2.5}$ mass. Figure 4 shows the temporal trends observed for sulphate, nitrate and ammonium and Fig. 6 shows the time series for the concentrations of these three components over the measurement period. Anthropogenic sulphate concentrations (where the fraction of marine sulphate has been removed) at MSY decreased by 43 % from 2002 to 2010 (α = 0.05). The EMEP Report 4/2011 reported a reduction in sulphur oxides (SO_x) emissions of 23 % in Spain from 2008–2009 alone, which would contribute to the reduction observed in secondary sulphate. Sulphate and V showed similar trends on a yearly basis (Fig. 6), with many intense peaks for both components coinciding. It is clearly visible that sulphate and V have decreased from 2008 onwards. Sulphate emissions are associated with fuel oil combustion for power generation and industry, as well as shipping. Vanadium and Nickel are also associated with these types of emissions and often correlate closely with sulphate measured at MSY. For the total measurement period, SO_4^{2-} correlates very well with V (R^2 = 0.74) and Ni (R^2 = 0.71). Thus, the decrease could be a result of reduced combustion emissions and the implementation of

emission abatement strategies, such as the IPPC directive (Directive 2008/1/EC), employed by industry and power plants. Power plants in Barcelona and the surrounding area began to phase out the use of fuel oil in exchange for natural gas, and by 2007 all power plants were using natural gas (Bruno et al., 2007). This may go some way to account for the reduction in these types of emissions observed since 2007.

Sulphate levels were highest during the summer; possibly as a result of enhanced photochemistry associated with more intense solar radiation, lower air mass renovation at a regional level, the increase in height of the summer mixing layer depth and higher regional transport, favouring the regional mixing of polluted air masses. Sulphate levels, along with many other components, undergo intense concentration increases under WAE (as described by Pey et al., 2010), These scenarios are associated with unseasonably warm and calm weather, with little advection, causing the local air mass to stagnate and pollution levels to increase over a period of days to entire weeks. Trend analysis on a seasonal basis did not show any significant trend, but the reductions observed from 2008 onwards are still pronounced.

Nitrate levels exhibited strong seasonal variability, giving highest concentrations during the colder winter months (especially during WAE), with minimum concentrations in summer. This trend is associated with the thermal instability of ammonium nitrate (Harrison and Pio, 1983; Querol et al., 2004), the most frequent form of nitrate at this site. These intense peaks of nitrate have been observed since measurements began, occurring from January to March, with secondary peaks sometimes registered in November. They are often followed by marked decreases in April, when WAE are less frequent and wetter weather is more prevalent. Since 2008, these winter nitrate episodes have diminished considerably. From 2002 to 2007, nitrate levels remained relatively consistent, but dropped sharply from 2008 onwards, as shown in Fig. 6. Trend analysis of annual nitrate levels have shown that the reduction has not followed such a linear pattern as OC or sulphate, but the reduction was still significant (α = 0.05), having reduced by 61 %. On a seasonal basis, statistically significant reductions of nitrate only occurred in winter (α = 0.05), very similar to the annual trend. As the majority of nitrate measured

at MSY occurred in winter, this similarity is to be expected. The seasonal evolution of nitrate for the remaining seasons did not display any significant trends. As the presence of ammonium nitrate varies with temperature (due to its thermal instability), the trends were not as pronounced during warmer seasons.

Yearly ammonium concentrations followed a relatively unusual trend as compared to nitrate and sulphate, with concentrations increasing year-on-year to 2005, followed by a sharp drop in 2006, maintaining a decreasing trend thereafter until 2010. The reduction was statistically significant (α = 0.05), giving a percentage decrease of 37 %. Ammonium underwent a bimodal seasonal variation, with intense winter peak concentrations during WAE, followed by generally elevated levels over the entire summer period. Ammonium measured on site was typically in the form of ammonium nitrate in the winter months and as ammonium sulphate during the warmer summer months, as will be discussed later. Ammonium did not show any significant trends on a seasonal basis, but a marked decrease since 2008 was observed.

3.4.4 Crustal and marine aerosols

As stated previously, crustal material and marine aerosol comprised 9 % and 2 % respectively of the total sum of the chemical components registered at MSY. Thus, marine aerosols did not influence the total $PM_{2.5}$ mass significantly. Elevated levels of crustal material are associated with high soil resuspension and episodes of Saharan dust intrusions (Pérez et al., 2008) i.e. they are mostly natural, and the crustal load of $PM_{2.5}$ increases significantly under NAF episodes. A minor decreasing trend has been observed for the crustal material measured at MSY (α=0.05), beginning in 2006 (Fig. 4). As mentioned previously. The unusual weather conditions experienced for the last two winters in the IP, as a result of the unusually negative NAO index, could be the cause for this slight reduction observed in crustal material. As stated previously, NAO can potentially control the frequency of Saharan dust intrusions reaching the IP, which would affect the mean crustal load concentrations. In addition, increased Atlantic Advection (associated with negative phases of the NAO) would have a cleaning effect

on the atmosphere. Indeed, marine aerosol registered a spike in annual concentrations in 2009 (0.5 $\mu g\,m^{-3}$). It could also be hypothesised that some part of the crustal material measured at MSY is a product of the construction industry. The construction industry in Spain has been especially hard-hit by the current economic recession, and crustal material produced by this industry may have contributed to the crustal load in $PM_{2.5}$. Analysis of seasonal trends of crustal material did not show any specific statistical trend. Marine aerosol is also of natural origin and, as expected, has not undergone any clear declining trend.

3.4.5 Trace elements

Various anthropogenic pollution tracers associated with industrial and traffic emissions (Pb, Cd, Cu, Sb, Sn, As, V, Cr, Ni, Co) and elements of natural origin (Li, Ti, Mn, Ga, Rb, Sr, La, Ce, Pr, Nd) were analysed for statistically significant trends and are listed in Table 3. Those experiencing the most statistically significant reductions (α = 0.01) are Cd, Sb, Sn and Pb, with a reduction ranging from 58–75 % since measurements began. Cu and As have recorded a reduction in the range of 44–51 % (α = 0.05), followed by Ni (α = 0.1) at 45 % and V at 41 %. Finally, Co underwent a reduction of 53 % (α = 0.05). Limit values are set by the European Union for Pb, (2008/50/CE) and target values are set for Cd, As, and Ni (2004/107/CE) and the reduction observed may be a direct result of the enforcement of this legislation. V, Ni and As all displayed peak concentrations in 2006 of 3 $ng\,m^{-3}$, 1.7 $ng\,m^{-3}$ and 0.3 $ng\,m^{-3}$ respectively, but from 2007 began to decrease in a similar fashion, as shown in Fig. 7. V and Ni are both associated with fuel oil combustion and correlate very well (R^2 = 0.64). Of the remaining trace elements, all have followed similar decreasing patterns over the measurement time period. Figure 6 shows typical anthropogenic pollution tracers Sn, Cu, Sb and Pb, all of which follow similar patterns over time, with many coinciding peaks in concentration (as occurs in September 2007, for example). In general they do not follow a clear seasonal trend. The variation of trace element concentrations at MSY during an intensive measurement campaign was described by Moreno et al. (2011), and outlined the inherent difficulty in

distinguishing exact sources of trace elements at MSY due to PM mixing and dilution during transport to MSY. The reductions and correlations between Pb and As (R^2 = 0.64) and Pb and Cd (R^2 = 0.62), all of which are regulated by legislation, suggest the efficacy of the abatement strategies and also that they may be of the same source, most likely industrial.

All the elements shown in Fig. 7 show a marked decrease in concentrations from 2008 onwards, quite possibly for the same reasons as those mentioned previously for the major PM components. V and Ni are tracers for the combustion of fuel oil and the reduction observed coincides with both the replacement of fuel oil in power generation with natural gas and also with the beginning of the economic recession. A similar study performed in Cantabria, in the north of Spain, has observed a similar effect, linking the effects of the economic recession to some industrial trace metal emissions (Arruti et al., 2011).

Some trace elements associated with crustal material (Li, Ti, Mn, Ga, Rb, Sr, La, Ce, Pr, and Nd) are also listed in Table 3. Some of these elements (Mn, Ga, Pr and Nd) have undergone statistically significant reductions similar to those observed for the total crustal material measured in $PM_{2.5}$. The percentage reductions observed for all the crustal elements are a result of the reduction observed in 2009 and 2010, as was the case for the crustal material, and the causes for this reduction are most likely the same.

On a seasonal basis, Pb exhibits a similar statistical trend for each season to that of its annual trend, with each season having α = 0.05 and a drop in ambient concentrations of Pb was recorded for each season from 2008 onwards. Cd also maintains the decreasing trend for each season with similar statistical significance (α = 0.01). Even though mean annual values of Cu and Sn show a reduction on a yearly basis, they do not undergo any apparent seasonal trend. Sb and As trend analysis shows a significant decreasing trend for spring and summer (α = 0.01) but in autumn and winter there is no perceptible trend.

3.5 Seasonal trends

It is difficult at MSY to ascertain the exact sources of pollutants measured at the site due to the mixed state of the aerosol during transport to the site, as stated previously. By analysing the seasonal variations in the chemical components it may be easier to identify the sources of pollutants. $PM_{2.5}$ and its chemical components are influenced by clear seasonal patterns and variations. To aid in the identification of the sources of the various chemical components, linear regression analysis was used comparing known tracers for both anthropogenic and natural components on a seasonal basis. Table 4 shows the correlation coefficients for the annual concentrations of various major components of $PM_{2.5}$ and various minor trace elements. The seasons for this study are defined as: winter (December, January, February and March), spring (April, May), summer (June, July, August) and autumn (September, October, November).

Sulphate exhibited year round correlation with the main tracers for fuel oil combustion such as V and Ni, as shown in Table 4, suggesting that these three components are from the same source and undergo linear changes in concentrations. The correlation between sulphate and NH_4^+ improves in the summer as ammonium at this time of year is most likely in the form of ammonium sulphate. The influence of intense winter pollution episodes and the mixed state of the aerosols arriving to MSY is highlighted by the correlation observed between sulphate and nitrate (R^2 = 0.74) in winter.

Nitrate, as explained earlier, displays a strong seasonal variability with elevated concentrations during the colder months due to the thermal instability of ammonium nitrate. Querol et al. (2009) reported that the ratio of $PM_{2.5}/PM_{10}$ nitrate in the colder months is almost 90 % at MSY, indicating only 10 % exists as coarse nitrate species (Ca and Na nitrate compounds). Thus, linear regression analyses could only be performed for winter, as levels are low in spring and autumn, and negligible in summer. However some relationship was observed between nitrate and ammonium in spring. Table 4 lists the correlation coefficients of nitrate with various components. In contrast to summer, ammonium was better correlated with nitrate in winter (R^2 = 0.83). During spring and

autumn, it can be reasonably assumed that ammonium exists as a mixture of both the nitrate and sulphate form (and possibly as organic ammonium, see below), depending on the meteorological conditions. Correlation was also observed with As (R^2 = 0.79), which is typically an anthropogenic element emitted by industrial practices, which may also be a source of nitrate at MSY. Finally, excellent anti-correlation was observed for nitrate and chlorine (R^2 = 0.90) indicating that Atlantic Advection episodes and marine breezes (containing high chlorine concentrations) have a cleaning effect at MSY, removing nitrate from the atmosphere.

Organic Carbon shows correlation with Pb for each season, improving in spring and summer, as shown in Table 4. In fact it is the only trace element that displayed consistent correlation with OC throughout the year. Why Pb (a specifically anthropogenic pollutant), as compared to the other tracers, correlated so well with OC is not clearly understood. Interestingly, OC had very good anti-correlation with marine aerosol components Na and Cl in winter (R^2 = 0.66 and 0.89, respectively), as observed previously with nitrate. Again, this was possibly due to the cleaning effect of Atlantic Advection and the influence of cleaner sea breezes from the nearby Mediterranean. The relationship between ammonium and OC was only evident in spring (April and May). It is possible that they were emitted independently in the same region, and arrived at MSY simultaneously. However it could also suggest that there is a significant source of organic ammonium (amines) that is specific to that time of year only. Few studies appear to exist on the importance of atmospheric amines and their sources. A review on atmospheric sources of amines by Xinlei Ge et al. (2011) lists many possible sources, including agriculture (livestock), industry, traffic, human waste, biomass burning and vegetation. Considering that the relationship between OC and NH_4^+ solely existed in spring indicates that the source was seasonally dependent. The presence of biomass burning in the surrounding area of MSY could well be the driving force behind this relationship. The burning of vegetation is strictly controlled in the area (to minimise risk of forest fires) and has a date limit after which it is prohibited, typically in late spring. Also, vegetative emissions of amines could also be important as MSY is densely forested,

and the seasonal activity of the surrounding trees and plant life may result in the release of amines to the atmosphere. Indeed, this is a new and unexpected discovery, and is worthy of further investigation.

4 Conclusions

The findings in this article provide good evidence that the implementation of pollution abatement strategies in Europe is having a direct effect on the levels of $PM_{2.5}$ and its various components. It is also hypothesised that the current economic climate, in recession since mid 2008 in Spain and many countries in Europe, is also affecting atmospheric pollutants through a reduction in activities associated with a healthy economy (increased road traffic, industrial processes, construction etc.). A reduction in $PM_{2.5}$ concentrations has been observed in Spain and across Europe. In most cases, this reduction has been gradual and consistent over time, implying the success of cleaner anthropogenic activities. Additional to this progressive trend, in some cases and especially for RB stations in the IP and Ispra in northern Italy, a dramatic decrease has been recorded since 2008, coinciding with the beginning of the economic crisis. The effect of the economic crisis on ambient trace element concentrations in northern Spain has also been observed (Arruti et al., 2011) and a reduction in black carbon owing to the economic crisis has been described in an urban area of south-east Spain (Lyamani et al., 2011). Indeed, Spain and Portugal, and to a lesser extent Italy, have all been especially affected by the current crisis, with specific industries such as the construction industry and employment suffering to a large extent.

Considering MSY as a representative site for the study of RB aerosols in the WMB, the temporal trends of the major and minor chemical components of $PM_{2.5}$ for a significant time-series of data were investigated. Temporal trends have shown that PM levels at MSY have been steadily decreasing over almost a decade, with statistical significance. The majority of this reduction in mass has been attributed to organic matter and secondary inorganic aerosol, the presence of which in the atmosphere is associ-

ated with anthropogenic emissions. Meanwhile, concentrations of marine aerosol have remained unchanged and crustal material has reduced only slightly. This is possibly a result of a decrease in anthropogenic mineral dust but also as a result of unusual meteorology recorded over the last few winter seasons. Intense periods of Atlantic Advection episodes as a result of unusually negative NAO may have had a cleaning effect on aerosols at MSY. Furthermore, the frequency of NAF episodes during winter appears to be influenced by the NAO, whereby positive (negative) episodes of NAO allow for more (less) frequent Saharan dust intrusions.

A similar reduction has been observed for many anthropogenic trace elements verifying this decreasing trend, and point to an ever improving situation regarding air quality. Many of these reductions, through statistical analysis using the Mann-Kendall test and Sen's estimate, have proven statistically significant over the past decade, meaning the reduction has been gradual and uniform.

In order to better understand the sources of the major and minor components that comprise $PM_{2.5}$, linear regression analyses were used to help define the possible sources of aerosols at MSY. The analysis was performed on a seasonal basis to investigate the changing source profiles and the effect of meteorology on aerosols on-site. Sulphate emissions were determined to be closely related with fuel oil combustion tracers V and Ni. Some of the reduction in ambient levels of sulphate, V and Ni may be related to the conversion of power plants employing fuel oil to natural gas, the last power plant having converted by 2008. Nitrate correlated closely with ammonium during the colder months, suggesting ammonium nitrate is the dominant compound of nitrate in winter. Finally, organic carbon correlated well with ammonium exclusively in spring, suggesting that amines may be an important source of organic carbon at MSY at certain times of year.

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References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Doherty, K., Ulbrich, I. M., Mohr, C., Kimmel, J.r., Sueper, D., Zhang, Q., Sun, Y., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, R., Prévôt, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478–4485, 2005.

Arruti, A., Fernández-Olmo, I., and Irabien, A.: Impact of the global economic crisis on metal levels in particulate matter (PM) at an urban area in the Cantabria Region (Northern Spain), Environ. Pollut., 159, 1129–1135, 2011.

Barmpadimos, I., Keller, J., Oderbolz, D., Hueglin, J., and Prévôt, A. S. H.: One decade of paralled fine (PM2.5) and coarse (PM_{10}–$PM_{2.5}$) particulate matter measurements in Europe: trends and variability. Atmos. Chem. Phys., 12, 3189–3203, doi:10.5194/acp-12-3189-2012, 2012.

Bruno, J., Pon, J., and Russi, D.: Report on Air Quality and Health: the cost of improvement of air quality (in Catalan). Generalitat de Catalunya, Departament de Medi Ambient i Habitatge, December 2007.

Gangoiti, G., Millán, M. M., Salvador, R., and Mantilla, E.: Long range transport and re-circulation of pollutants in the Western Mediterranean during the RECAPMA-Project, Atmos. Environ., 35, 6267–6276, 2001.

Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines-Part 1. A review, Atmos. Environ., 45, 524–546, 2011.

Gilbert, R. O.: Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold, New York, USA, 1987.

Harrison, R. M. and Pio, C.: Size differentiated composition of inorganic aerosol of both marine and continental polluted origin, Atmos. Environ., 17, 1733–1738, 1983.

Querol, X., Alastuey, A., Viana, M. M., Rodríguez, S., Artíñano, B., Salvador, P., Santos, S. G. D., Patier, R. F., Ruiz, C. R., Rosa, J. D. L., Campa, A. S. D. L., Menedez, M., and Gil, J. I.: Speciation and origin of PM_{10} and PM2.5 in Spain, J. Aerosol Sci., 35, 1151–1172, 2004.

Hurrell, J., Kushnir, Y., Otterson, G., and Visbeck, M.: An overview of the north Atlantic oscillation. The North Atlantic Oscillation: climate significance and environmental impact. Geophys. Monogr., 134, 1–35, 2003.

Hurrell, J. and Deser, C.: North Atlantic climate variability: the role of the North Atlantic oscillation, J. Mar. Syst., 78, 28–41, 2009.

IPCC: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the IPCC, ISBN 978 0521 88009-1 Hardback; 978 0521 70596-7 Paperback, 2007.

Jorba, O., Pérez, C., Rocadenbosch, F., and Baldasano, J. K.: Cluster Analysis of 4-Day Back Trajectories Arriving in the Barcelona Area (Spain) from 1997 to 2002, J. Appl. Meteorol, 43, 887-901, 2004.

Lyamani, H., Olmo, F. J., Foyo, I., and Alados-Arboledas, L.: Black carbon aerosols over an urban area in south-eastern Spain: Changes detected after the 2008 economic crisis, Atmos. Environ., 45, 6423–6432, 2011.

Millán, M., Salvador, R., Mantilla, E., and Kallos, G.: Photo-oxidant dynamics in the Mediterranean basin in summer: results from European research projects, J. Geophys. Res., 102, 8811–8823, 1997.

Minguillón, M. C., Perron, N., Querol, X., Szidat, S., Fahrni, S. M., Alastuey, A., Jimenez, J. L., Mohr, C., Ortega, A. M., Day, D. A., Lanz, V. A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco. R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J. F., Baltensperger, U., Prévôt, A. S. H.: Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain, Atmos. Chem. Phys., 11, 12067–12084, doi:10.5194/acp-11-12067-2011, 2011.

Moreno, T., Querol, X., Alastuey, A., Reche, C., Cusack, M., Amato, F., Pandolfi, M., Pey, J., Richard, A., Prévôt, A. S. H., Furger, M., and Gibbons, W.: Variations in time and space of trace metal aerosol concentrations in urban areas and their surroundings, Atmos. Chem. Phys., 11, 9415–9430, doi:10.5194/acp-11-9415-2011, 2011.

Moulin, D., Lambert, C. E., Dulac, F., and Dayan, U.: Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation, Nature, 387, 691–694, 1997.
Peñuelas, J., Llusia, J., and Gimeno, B. S.: Effects of ozone concentrations on biogenic volatile organic compounds emission in the Mediterranean region, Environ. Pollut., 105, 17–23, 1999.
Pérez, C., Sicard, M., Jorba, O., Comeron, A., andBaldasano, J. K.: Summertime re-circulations of air pollutants over the north-eastern Iberian coast observed from systematic EARLINET lidar measurements in Barcelona, Atmos. Environ., 38, 3983–4000, 2004.
Pérez, N., Pey, J., Castillo, S., Viana, M., Alastuey, A., and Querol, X.: Interpretation of the variability of levels of regional background aerosols in the Western Mediterranean. Sci. Total Environ., 407, 524–540, 2008.
Pey, J., Pérez, N., Castillo, S., Viana, M., Moreno, T., Pandolfi, M., López-Sebastián, J.M., Alastuey, A., and Querol, X.: Geochemistry of regional background aerosols in the Western Mediterranean, Atmos. Res., 94, 422–435, 2009.
Pey, J., Pérez, N., Querol, X., Alastuey, A., Cusack, M., and Reche, C.: Intense winter pollution episodes affecting the Western Mediterranean. Sci. Total Environ., 408, 1951–1959, 2010.
Pope, C. A. and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect. J. Air. Waste Manage., 56, 709–742, 2006.
Querol, X., Alastuey A., Puicercus, J. A., Mantilla, E., Ruiz, C. R., Lopez-Soler, A., Plana, F., and Artíñano, B.: Seasonal evolution of suspended particles around a coal-fired power station: particulate levels and sources. Atmos. Environ., 32, 719–731, 1998a.
Querol, X., Alastuey A., Puicercus, J. A., Mantilla, E., Ruiz, C. R., Lopez-Soler, A., Plana, F., and Artíñano, B.: Seasonal evolution of suspended particles around a coal-fired power station: particulate levels and sources, Atmos. Environ., 32, 1963–1978, 1998b.
Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Mantilla, E., and Ruiz, C. R.: Monitoring of PM_{10} and $PM_{2.5}$ around primary particulate anthropogenic emission sources, Atmos. Environ., 35, 845–858, 2001.
Querol, X., Pey, J., Minguillón, MC., Pérez, N., Alastuey, A., and Viana, M.: PM speciation and sources in Mexico during the MILAGRO-2006 Campaign. Atmos. Chem. Phys., 8, 111–128, doi:10.5194/acp-8-111-2008, 2008.
Querol, X., Alastuey, A., Pey, J., Cusack, M., Pérez, N., Mihalopoulos, N., Theodosi, C., Gerasopoulos, E., Kubilay, N., and Koçak, M.: Variability in regional background aerosols

within the Mediterranean. Atmos. Chem. Phys., 9, 4575–4591, doi:10.5194/acp-9-4575-2009, 2009.
Rodríguez, S., Querol, X., Alastuey, A., and Mantilla, E.: Origin of high PM10 and TSP concentrations in summer in Eastern Spain, Atmos. Environ., 36, 3101–3112, 2002.
Rodríguez, S., Querol, X., Alastuey, A., Viana, M., and Mantilla E.: Events affecting levels and seasonal evolution of airborne particulate matter concentrations in the Western Mediterranean, Environ. Sci. Technol., 37, 216–222, 2003.
Salmi, T., Määttä, A., Anttila, P., Ruoho-Airola, T., and Amnell, T.: Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates-the Excel template application MAKESENS, In publications on Air Quality No. 31 (ed. Finnish Meteorological Institute), Finnish Meteorological Institute, p. 35, 2002.
Seco, R., Peñuelas, J., Filella, I., Llusià, J., Molowny-Horas, R., Schallhart, S., Metzger, A., Müller, M., and Hansel, A.: Contrasting winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions, Atmos. Chem. Phys., 11, 13161–13179, doi:10.5194/acp-11-13161-2011, 2011.
Soriano, C., Baldasano, J. M, Buttler, W. T., and Moore, K.: Circulatory Patterns of Air Pollutants within the Barcelona Air Basin in a summertime situation: Lidar and Numerical Approaches, Bound.-Lay. Meteorol., 98, 33–55, 2001.
Tsyro, S., Yttri, K. E., and Aas, W.: Measurement and model assessment of particulate matter in Europe, 2009. EMEP Transboundary particulate matter in Europe Status Report, 4/2011, 23–52, 2011.
Turpin, B. J. and Lim, H. J.: Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 602–610, 2001.
Vicente-Serrano, M. S., Trigo, M. R., López-Moreno, J. I., Liberato, M. L. R., Lorenzo-Lacruz, J., Beguería, S., Morán-Tejeda, E., and El Kenawy, A.: Extreme winter precipitation in the Iberian Peninsula 2010: anomalies, driving mechanisms and future projections. Clim. Res., 46, 51–65, 2011.
Visbeck, M. H., Hurrell, J. W., Polvani, L., and Cullen, H. M.: The North Atlantic Oscillation: past, present and future, PNAS, 98, 12876–12877, 2001.

Table 1. Location of the various monitoring sites, their respective altitude (meters above sea level), $PM_{2.5}$ concentration for corresponding first year and last year of measurements, average $PM_{2.5}$ ($\mu g\,m^{-3}$) and standard deviation. (EMEP stations in bold).

Country	Site	Latitude	Longtitude	m.a.s.l.	Period (years)	$PM_{2.5}$ (First Year)	$PM_{2.5}$ (Last Year)	$PM_{2.5}$ Mean±Stan.Dev
Spain	**Montseny***	41°46′ N	02°21′ E	720	2002–2010	14.0	8.9	12.6±2.2
	Cabo de Creus**	42°19′ N	00°05′ E	23	2002–2010	12.9	7.9	10.8±2.7
	Els Torms**	41°23′ N	00°43′ E	470	2002–2010	10.0	7.3	10.2±2.1
	Zarra**	39°05′ N	01°06′ W	885	2002–2010	8.2	5.5	7.4±1.2
	Viznar**	37°14′ N	03°28′ W	1265	2002–2010	10.3	9.2	10.1±0.7
	Barcarrota**	38°28′ N	06°55′ W	393	2002–2010	12.5	7.6	8.8±2.0
	O Saviñao**	42°28′ N	07°42′ W	506	2002–2010	9.4	6.2	8.1±1.4
	Niembro**	43°26′ N	04°50′ W	134	2002–2010	10.1	9.2	9.8±1.0
	Campisábalos**	41°16′ N	03°08′ W	1360	2002–2010	7.0	5.7	6.9±0.9
	Peñausende**	41°17′ N	05°52′ W	985	2002–2010	8.0	4.9	6.9±1.3
	Risco Llano**	39°31′ N	04°21′ W	1241	2002–2010	6.7	5.9	7.1±1.0
Austria	**Illmitz****	47°46′ N	16°45′ E	117	2002–2010	23.3	19.0	19.7±3.2
Italy	**Ispra****	45°48′ N	08°38′ E	209	2002–2009	29.4	19.2	26.2±4.2
Switzerland	**Payerne****	46°48′ N	06°56′ E	489	2002–2010	15.9	10.6	14.5±3.0
Germany	Pfälzerwald-Hortenkopf***	49°16′ N	07°49′ E	606	2003–2009	12.6	9.0	9.7±1.5
	Schwartenberg***	50°39′ N	13°27′ E	785	2002–2009	10.5	8.7	9.5±2.0
	Schauinsland**	47°54′ N	07°54′ E	1205	2002–2009	10.2	6.9	7.2±1.7
	Waldhof**	52°48′ N	10°45′ E	74	2003–2009	16.5	11.8	13.5±2.3
Finland	Virolahti***	60°31′ N	27°40′ E	4	2004–2009	7.5	5.5	6.6±1.1
	Utö***	59°46′ N	21°22′ E	7	2004–2009	6.7	5.3	5.9±0.7
	Hyytiälä**	61°51′ N	24°17′ E	181	2002–2009	7.5	3.8	5.5±1.3
Sweden	**Vavihill****	56°01′ N	13°08′ E	163	2002–2010	10.5	7.2	9.9±2.2
	Aspvreten**	58°48′ N	17°22′ E	25	2002–2010	8.9	5.7	7.5±1.3
Norway	**Birkenes****	58°23′ N	08°15′ E	190	2002–2010	6.0	3.4	4.3±1.1
Portugal	Fundão***	40°08′ N	07°10′ W	473	2005–2010	9.9	6.9	8.3±1.8
	Chamusca***	39°12′ N	08°16′ W	43	2003–2010	10.3	9.1	10.8±2.1
	Lamas de Olo***	41°22′ N	07°47′ W	1086	2004–2010	11.0	3.6	9.0±4.1
	Ervedeira***	40°35′ N	08°40′ W	32	2006–2010	13.9	11.9	10±2.8

* This study; ** EMEP; *** Airbase, the European Air Quality Database (http://acm.eionet.europa.eu/databases/airbase/).

Table 2. Percentage reduction of $PM_{2.5}$ and statistical significance of the decreasing trend (α) for various stations across Europe.

Site	First year	Last year	# data points	α	% reduction
Montseny	2002	2010	9	0.01	35
Cabo de Creus	2002	2010	9	0.001	49
Els Torms	2002	2010	9	0.05	40
Zarra	2002	2010	9	–	30
Viznar	2002	2010	9	–	14
Barcarrota	2002	2010	9	0.05	41
O Saviñao	2002	2010	9	0.01	36
Niembro	2002	2010	9	–	7
Campisábalos	2002	2010	9	0.05	34
Peñausende	2002	2010	9	0.001	42
Risco Llano	2002	2010	9	–	20
Illmitz	2002	2010	9	–	31
Payerne	2002	2010	9	0.05	36
Vavihill	2002	2010	9	0.05	35
Aspvreten	2002	2010	9	0.05	34
Birkenes	2002	2010	9	–	41

Table 3. Percentage reduction of various trace elements, mean concentration (ng m^{-3}) and statistical significance of the decreasing trend (α) recorded at MSY (elements with statistically significant reductions in bold).

Element	Measurement Period	Mean Conc. (ng m^{-3})	α	% reduction
Pb	2002–2010	3.82±1.41	0.01	67
Cd	2002–2010	0.13±0.06	0.01	75
Cu	2004–2010	2.52±0.69	0.05	44
Sb	2004–2010	0.29±0.13	0.01	58
Sn	2004–2010	0.76±0.32	0.01	58
As	2002–2010	0.22±0.06	0.05	51
V	2002–2010	2.11±0.57	–	41
Cr	2002–2010	0.82±0.20	–	34
Ni	2002–2010	1.22±0.34	0.1	45
Co	2002–2010	0.06±0.02	0.05	53
Li	2002–2010	0.06±0.02	–	43
Ti	2002–2010	3.51±1.19	–	34
Mn	2002–2010	1.94±0.49	0.1	37
Ga	2002–2010	0.04±0.02	0.1	53
Rb	2002–2010	0.14±0.03	–	43
Sr	2002–2010	0.47±0.26	–	49
La	2002–2010	0.07±0.01	–	34
Ce	2002–2010	0.13±0.02	–	17
Pr	2002–2010	0.02±0.01	0.05	46
Nd	2002–2010	0.06±0.02	0.1	49

Table 4. Regression analysis of SO_4^{2-} vs. various major and minor components of $PM_{2.5}$ for the different seasons.

Winter		Spring	
Component	R^2	Component	R^2
SO_4^{2-} – V	0.70	SO_4^{2-} – V	0.76
SO_4^{2-} – Ni	0.65	SO_4^{2-} – Ni	0.82
SO_4^{2-} – NH_4^+	0.60	SO_4^{2-} – NH_4^+	0.62
SO_4^{2-} – NO_3^-	0.74		
NO_3^- – NH_4^+	0.83	NO_3^- – NH_4^+	0.43
NO_3^- – As	0.79		
NO_3^- – Cl^-	0.90		
OC – Pb	0.53	OC – Pb	0.70
OC – Cl^-	0.89	OC – NH_4^+	0.76
OC – Na	0.66		
Summer		**Autumn**	
Component	R^2	Component	R^2
SO_4^{2-} – V	0.60	SO_4^{2-} – V	0.74
SO_4^{2-} – Ni	0.79	SO_4^{2-} – Ni	0.70
SO_4^{2-} – NH_4^+	0.76	SO_4^{2-} – NH_4^+	0.80
OC – Pb	0.71	OC – Pb	0.63
OC – Fe	0.70		

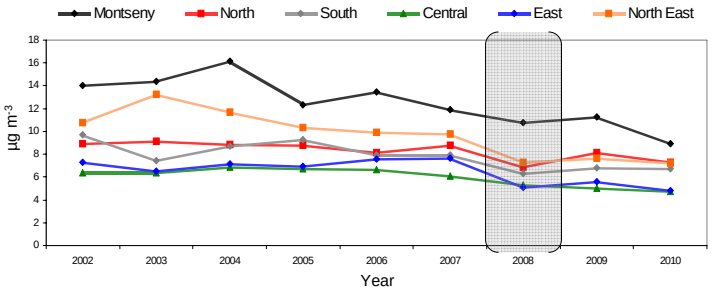

Fig. 1. $PM_{2.5}$ concentrations measured at RB sites across Spain from 2002–2010 (year of most significant decrease highlighted).

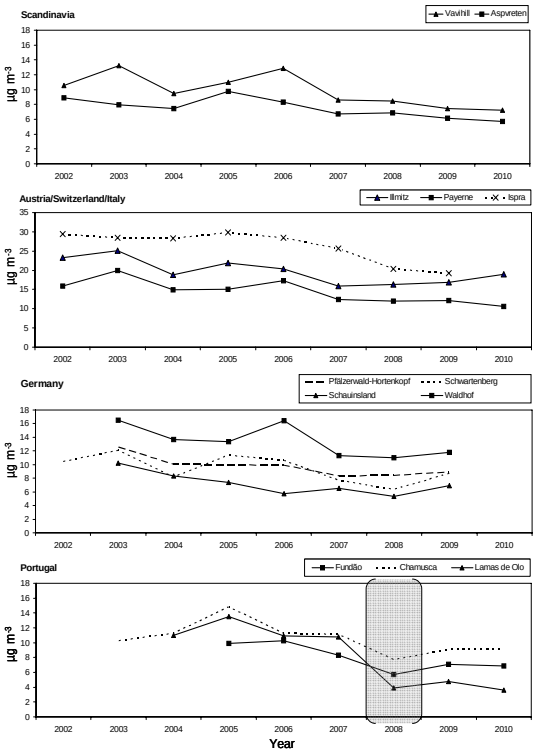

Fig. 2. $PM_{2.5}$ levels measured for various RB stations across Europe according to AIRBASE and EMEP data (year of most significant decrease highlighted in grey).

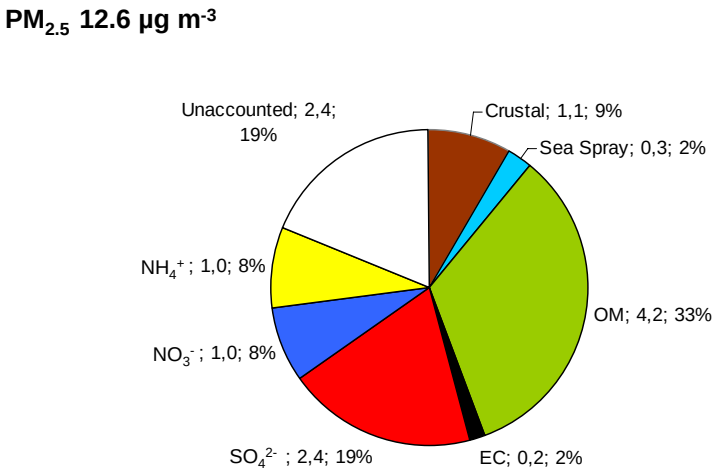

Fig. 3. Mean $PM_{2.5}$ composition ($\mu g\,m^{-3}$) at MSY for the study period (2002–2010).

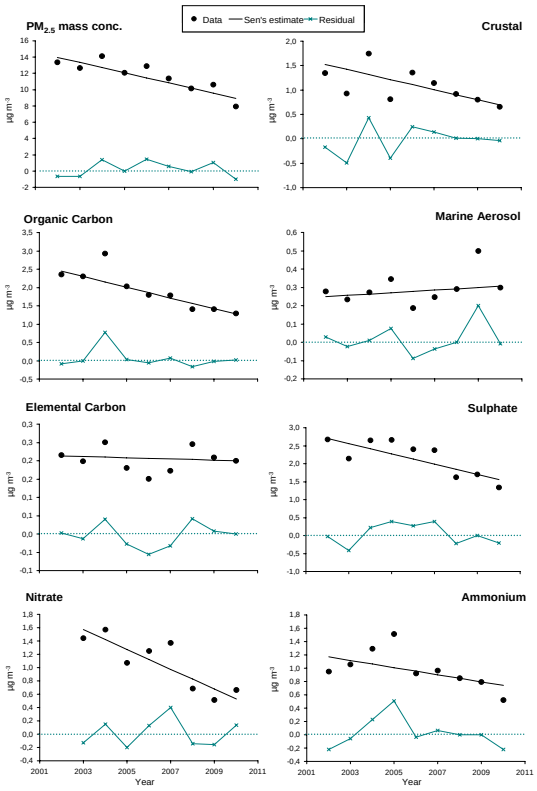

Fig. 4. Temporal trends for $PM_{2.5}$ and its various major chemical components by means of the Mann-Kendall test and Sen's method using MAKESENS (Salmi et al., 2002).

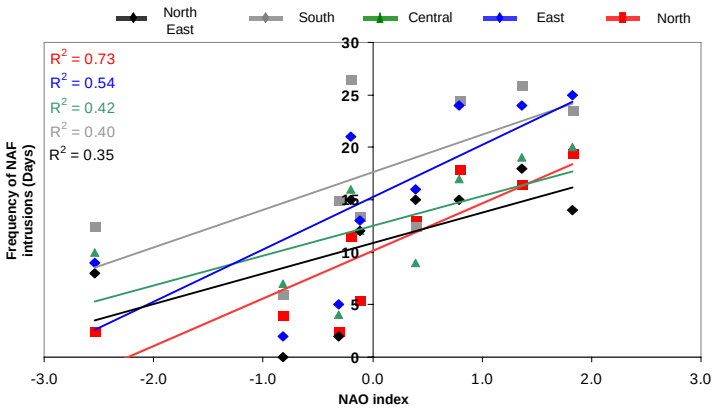

Fig. 5. Correlation plot of NAO index and the frequency of Saharan dust intrusions (NAF) in days during winter for 2002–2010 for different regions of Spain.

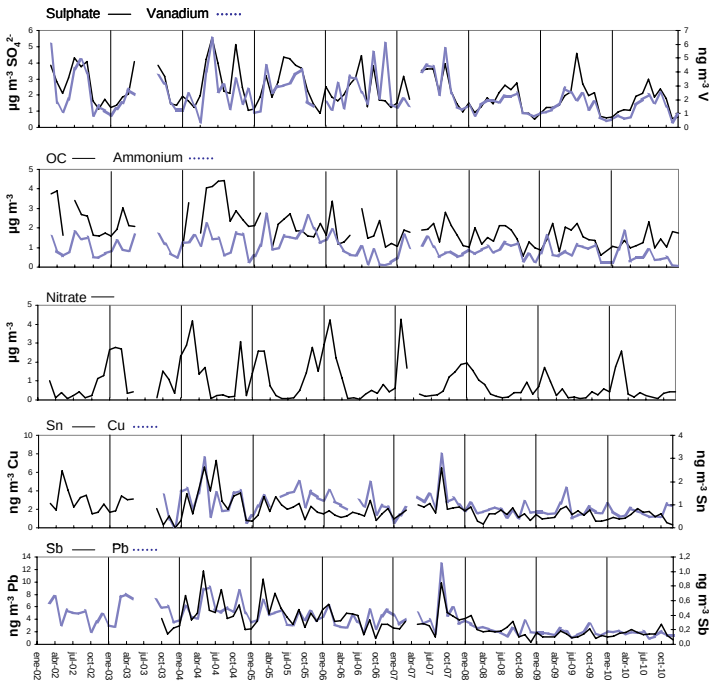

Fig. 6. Time evolution of concentration levels of SO_4^{2-}, V, OC, NH_4^+, NO_3^-, Cu, Sn, Pb and Sb at MSY.

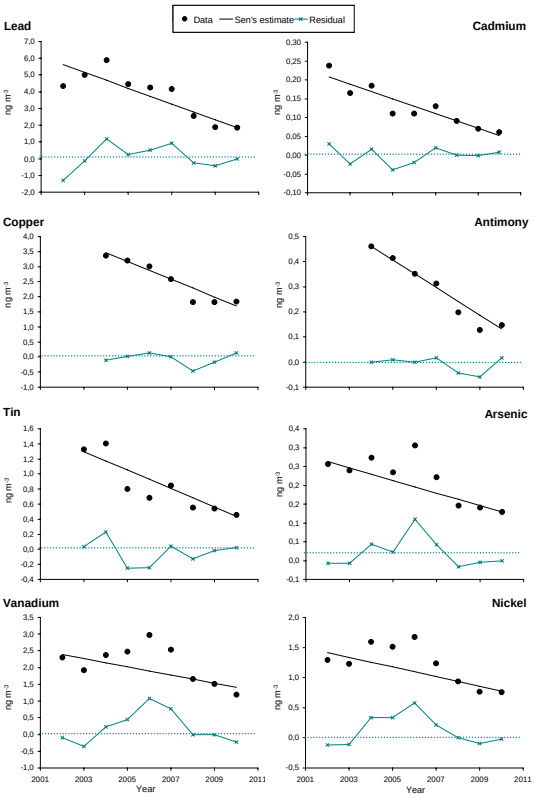

Fig. 7. Temporal trends for a selection of trace anthropogenic chemical components by means of the Mann-Kendall test and Sen's method using MAKESENS (Salmi et al., 2002).