

## Comparison of temporal features of sulphate and nitrate at urban and rural sites in Spain and the UK

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### H I G H L I G H T S

- ▶ Aerosol nitrate and sulphate patterns are compared seasonally in Madrid and London.
- ▶ Results show the dominant processes affecting their formation and evolution.
- ▶ Weekly analysis show weekend reductions for nitrate in summer and sulphate in winter.
- ▶ Daily evolution of nitrate is heavily influenced by meteorological factors.
- ▶ Strong differences seen emphasises the need to study cities individually.

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### A B S T R A C T

A seasonal comparison of aerosol secondary inorganic component (SIC) patterns on annual, weekly and daily timescales has been performed at urban Madrid and London and at rural sites in the central Iberian Peninsula and south-eastern UK alongside data for precursor gases. A database from winter 2004 to summer 2011 has been analysed. Results show the dominant processes affecting the formation and evolution of nitrate ( $\text{NO}_3^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) in both regions. In Madrid, photochemistry dominates formation of nitrate, which is mostly locally-generated. Strong thermal decomposition results in very low concentrations in summer. In contrast, in London high nocturnal values suggest the importance of heterogeneous formation processes as well as nitrate condensation at lower temperatures. The seasonal nitrate maximum in the UK is found in late winter-early spring, when the region typically receives the highest input of pollutants transported from mainland Europe. Daily evolution of nitrate in both cities is heavily influenced by meteorological factors. Seasonal sulphate patterns show no obvious trend, except at the Spanish rural site in summer where photochemical formation was apparent. In Madrid, daily  $\text{SO}_2$  and sulphate patterns exhibiting maximum concentrations at noon were found in winter. In previous studies this phenomenon was observed for  $\text{SO}_2$  in London, where it was explained by the entrainment of pollutants from aloft into the mixing layer. SIC weekend reductions were investigated at the urban background sites of Madrid and London, and in both cities statistically significant fine nitrate reductions of around 20% are found in summer. These values are consistent with the annual reductions observed by researchers in the US. Weekend sulphate reductions occurred in winter, reflecting a clear impact of anthropogenic sulphate in urban environments, in spite of the large reductions in sulphur emissions in Europe in the last decade. Ratios of nitrate and sulphate to oxidant gases and to one another have been calculated for Madrid, and are consistent with a contribution of local formation to sulphate in winter, while in summer a regional background unrelated to urban  $\text{SO}_2$  is observed. The strong differences in the behaviour seen in London and Madrid (and the rural sites) emphasises the need to study cities individually and not to extrapolate conclusions drawn in one city to others in different climate/topographic situations.

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### 1. Introduction

Secondary inorganic aerosol is the result of transformation processes of primary pollutants in the atmosphere which depend on emissions as well as on meteorology. Such pollutants can be transported from the source region to thousands of km away, which

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means that an interpretation of aerosol behaviour in a zone not only requires information on sources and pathways in that region but also on pollutants transported from other source areas.

Both meteorology and emissions show large differences in different regions of Europe, and conclusions from a certain region cannot be extrapolated to other parts of the continent. A compendium of European aerosol phenomenology including chemical characteristics of particulate matter at kerbside, urban, rural and background sites is presented in Putaud et al. (2004) and Putaud et al. (2010). Querol et al. (2004) analysed PM characteristics of seven European regions comparing levels and speciation studies of PM<sub>10</sub> and PM<sub>2.5</sub>. They found in Central Europe (including UK) annual mean values of SIC slightly higher than those found in Southern Europe, where the difference between rural and urban sites was larger. It was noticeable that SIC levels were very similar in all urban areas, with an extra input in intensively industrialised regions or heavily polluted urban areas. Regarding long-range transport, Borge et al. (2007) found very different and characteristic transport patterns that affected PM<sub>10</sub> concentrations in three European cities: Athens, Madrid and Birmingham.

The joint analysis of pollutant and meteorological data on different timescales provides information on the dominant processes that govern aerosol formation and transport. Competing effects lead to different patterns in different locations. Nitrate in the fine fraction, mainly ammonium nitrate, is partitioned into a gaseous and a particulate phase, this partition depending on temperature. As sulphate and coarse nitrate are more thermally and chemically stable, they are more affected by transport processes, whereas fine nitrate evolution is expected to be more affected by local meteorology and formation/dissociation processes.

Time evolution of pollutants on a yearly timescale reveals a seasonal pattern related to emissions and climate. Weekday/weekend analysis provides information on the formation and accumulation time of secondary pollutants in the atmosphere, but moreover, since there is no natural process which follows a seven day cycle, it can provide information on the anthropogenic influence on a certain site. The daily pattern not only gives us information about the origin of pollutants, since a marked anthropogenic emission pattern indicates anthropogenic local/regional provenance, but also on the formation processes involved. In the last decade, several researchers have analysed aerosol behaviour on different timescales. Rattigan et al. (2006) reported fine nitrate and sulphate seasonal patterns in a rural and an urban site in the state of New York, finding maximum sulphate concentrations in the warmer months, and highest nitrate in the colder periods. They concluded that photochemistry was the dominant formation mechanism for sulphate aerosol, while nitrate concentration was driven by thermal dissociation of ammonium nitrate. Millstein et al. (2008) investigated the fine particle nitrate response to weekly changes in emissions at four US urban sites. They found a reduction in measured concentrations of PM nitrate on weekends associated with lower NO<sub>x</sub> emissions, indicating the potential to reduce PM<sub>2.5</sub> nitrate via NO<sub>x</sub> control. Recently, Bampardimos et al. (2011) investigated the weekly cycle of coarse and fine mode PM in different types of rural and urban stations in Switzerland to calculate the contribution of traffic to the coarse mode urban ambient concentrations. Wittig et al. (2004) studied diurnal patterns of nitrate and sulphate on a seasonal base at the Pittsburgh Supersite, relating features of the patterns to temperature, RH, and ultraviolet radiation that affected the formation processes of secondary aerosol.

In this paper we perform a comparison of the temporal features of nitrate and sulphate in the south-eastern UK and the central part of the Iberian Peninsula. Results from five sites, including urban background sites in the two capitals, Madrid and London, and

nearby rural sites are presented. This study aims to elucidate the processes that dominate the formation and evolution of SIC in winter and summer in the two European cities.

## 2. Sampling sites and techniques

### 2.1. Meteorology and topography

The Madrid air basin is located in the central part of the Iberian Peninsula. The area is characterized by an extended plateau. The Metropolitan Area is bordered to the north–northwest by a high mountain range (Sierra de Guadarrama) 40 km from the city, and to the northeast and east by lower mountainous terrain. The weather in Madrid is typical of a mid-latitude continental area, with hot dry summers and cold winters. The general synoptic situation leading to the occurrence of episodic events corresponds in winter to stagnant anticyclonic conditions, with the usual formation of nocturnal surface inversions. In summer, the mixed layer evolution is quite different, because of the development of strong thermal convective activity. The influence of the mountains produces characteristic circulations.

The geography of south-eastern England consists of lowland terrain, with heights not exceeding 400 m. The main meteorological influence is the proximity to the Atlantic Ocean, which results in a humid and windy maritime climate, subject to frequent changes.

Climatic information can be obtained from the meteorological services of both countries (<http://www.aemet.es/es/serviciosclimaticos> and <http://www.metoffice.gov.uk/climate/uk/>). Seasonal comparison of relevant meteorological parameters averaged from 1971 to 2000 shows important differences that are likely to influence aerosol formation and transformation. Mean temperatures are higher in Madrid than London, but the difference is larger in summer (6–8 °C in Madrid and 4–5 °C in London in winter; 20–25 °C Madrid and around 17 °C London in summer). However, sunshine and precipitation make the largest differences. Sunshine in winter is around 425 h in Madrid and 170 in London, while in summer it reaches 1000 h in Madrid and 600 in London. On the other hand, average rainfall is 130 mm in winter and only 30 mm in summer in Madrid, while precipitation in southern England is over 200 mm in both seasons.

Since the Spanish rural site is significantly elevated above the level of the city (see Fig. 1), meteorological features are different. The wind regime is affected by the mountainous topography. Temperatures are lower and mean precipitation is higher. In contrast, climatic differences between the UK sites are small.

### 2.2. Spain sites and measurements

The metropolitan area of Madrid has more than 6 million inhabitants and more than 2.5 million residents live in the surrounding towns. It comprises a car fleet over 4 million vehicles (fifty percent of which are diesel powered, including more than six hundred thousand medium- and heavy-duty trucks) with very intense traffic on weekdays on the connecting radial roads and the several existing ring roads. Emissions from light industry and domestic heating in winter contribute to a lesser extent. Gas boilers are the predominant domestic heating devices, while fuel-oil and coal boilers are also present but in a much lower percentage. These features, together with the long distance between the Madrid metropolitan area and other significant urban or industrial areas in central Spain (around 200 km), allow study of local influences.

One of the sampling sites was located within the CIEMAT facilities in the north western area of the city of Madrid (40° 27.5'N, 3° 43.5'W, 669 m asl). This site is representative of urban

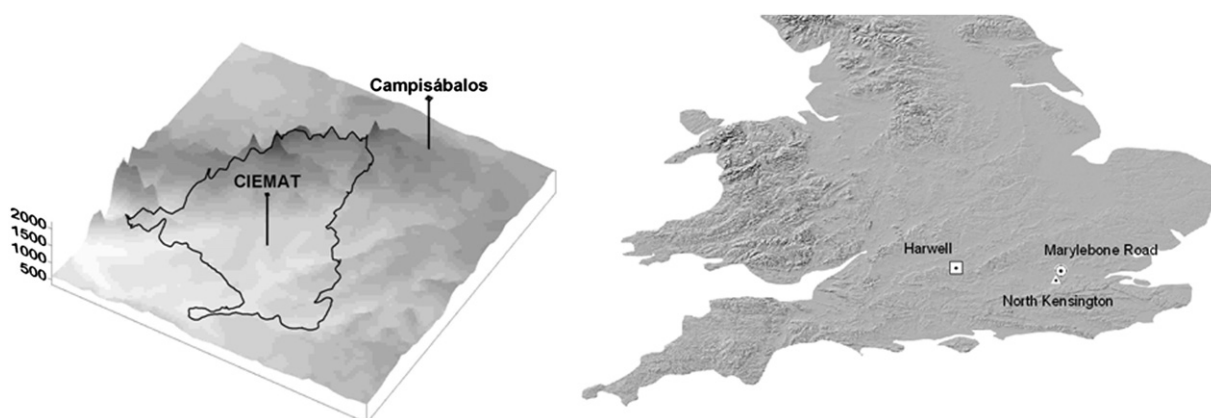


Fig. 1. Topographic maps of the two regions.

background conditions. It is located in the north-west section of the city, close to the outskirts of the city in an area largely covered by vegetation but with some heavily trafficked roads (none close to the sampler).

Gaseous pollutants, particulate SIC concentrations and meteorological parameters were continuously recorded.

The rural site selected for this study is Campisábalos, a regional background monitoring site included in the air quality network of the European Monitoring and Evaluation Programme (EMEP). This site is located in the center of the Iberian Peninsula ( $41^{\circ} 17' N$ ,  $3^{\circ} 09' W$ , 1360 m asl), on the far north-eastern limit of the Madrid air basin and 100 km away from the city. It is surrounded mainly by coniferous forest and in a small proportion by farmland and pasture. PM10 filters are collected daily and analysed for ions. Temperature and insolation data were collected from the Spanish Meteorological Service (AEMET) station in Puerto de Navacerrada ( $40^{\circ} 46.83' N$ ,  $4^{\circ} 0.62'$ , 1894 m asl).

### 2.3. UK sites and measurements

UK data have been obtained for sites that form part of the UK Automatic Urban and Rural Network (AURN) and the London Network.

With a population over 7 million inhabitants, London is by far the largest city in the UK.

The Marylebone Road monitoring station ( $51^{\circ} 32.6' N$ ,  $0^{\circ} 9.92' W$ , 27 m asl) is one of the sites selected for this study. It is located on the kerbside of a major arterial route within the City of Westminster in London. Traffic flows of over 80 000 vehicles per day pass the site on 6 lanes with frequent congestion.

North Kensington ( $51^{\circ} 31.27' N$ ,  $0^{\circ} 12.8' W$ ) is an urban background site located in a residential area to the west of central London, approximately 4 km from the Marylebone Road site. The nearest road is approximately 30 m from the station with an average daily traffic flow of 8000 vehicles per day. There are a number of retail and light industrial units located within the vicinity to the east and west of the monitoring station.

The Harwell rural site ( $51^{\circ} 34.72' N$ ,  $1^{\circ} 20.26' W$ , 137 m asl) is also an EMEP site and is located within the grounds of the Harwell Science Centre, in the middle of an unfarmed field and surrounded by predominantly agricultural land. It is around 85 km from London. There is limited activity in the area. Distant sources include the busy A34 dual carriageway about 2 km to the east and the Didcot power station about 5 km to the north-east. A careful analysis of the influence of the power station has shown that it accounts for only 3.3% of the annual mean sulphur dioxide measured at Harwell (Jones and Harrison, 2011).

These sites are equipped with continuous monitors recording fine nitrate concentration and gases. PM10 filters are collected daily and analysed for ions.

### 2.4. Techniques

#### 2.4.1. Spain

Fine nitrate concentration was measured using a Rupprecht and Patashnick 8400N Nitrate Analyser with a PM2.5 sampling inlet (Long and McClenny, 2006) on a 10-min time basis.

Semi-continuous PM1 sulphate concentration was registered with a Thermo 5020 sulfate particulate analyzer (SPA) (Schwab et al., 2006) on a time basis of 20 min. Both instruments were successfully compared to filter-based measurements. Gaseous species ( $SO_2$ ,  $NO$  and  $NO_2$ ) at the CIEMAT site were measured by a DOAS spectrometer (OP-SIS AR-500) along a 228 m horizontal path with a mean height of 10 m above ground. The measurement frequency was similar to the particulate nitrate instrument. Meteorological information was obtained from a permanent tower installed at CIEMAT with temperature at 4 m. Data were recorded every 10 min. At Campisábalos, PM10 filters are collected with an Andersen GUV15H, and particulate sulfate and nitrate concentrations are determined by Ion Chromatography (IC).

#### 2.4.2. UK

Fine nitrate concentration was measured using a Rupprecht and Patashnick 8400N Nitrate Analyser with a PM2.5 sampling inlet. Gaseous nitrogen oxides in the UK sites are measured hourly using the chemiluminescence technique. Gaseous  $SO_2$  is measured by UV fluorescence. Filters at UK sites are collected using a Partisol sampler with a PM10 inlet and analysed for ions by IC. Meteorological data in the UK have been obtained from London Heathrow ( $51^{\circ} 28.74' N$ ,  $0^{\circ} 26.94' W$ , 25 m asl) which lies between the London sites and Harwell.

All plots use UTC time and averages have been computed if 50% of the data was captured over the averaging interval. Error bars are based on 95% confidence intervals (CI) of the mean.

## 3. Results

### 3.1. Annual patterns

Monthly averages have been computed to obtain a seasonal pattern for nitrate and sulphate in four sampling sites. Six years of data (2005–2010) have been computed except for the sulphate in Madrid, where available data started in June 2009. Due to this fact and the significant differences found in these three years,

measurement periods were plotted separately. In London, the site selected to calculate the seasonal evolution is Marylebone Road due to the higher data availability. A comparison with the urban background site did not show significant differences in the nitrate and sulphate monthly means (see Supplementary information for North Kensington).

In central Spain, the highest nitrate monthly means are around  $3 \mu\text{g m}^{-3}$  at the urban background site and three times lower at the rural site. The sulphate concentrations show smaller differences, being below  $2.5 \mu\text{g m}^{-3}$ . In London and also at the rural Harwell site the fine nitrate monthly means are above the Madrid concentrations, reaching  $4 \mu\text{g m}^{-3}$ . PM10 nitrate and sulphate concentrations in Harwell are smaller than in London, but well above Campisábalos.

The behaviour of pollutants at both Spanish sites is very different, unlike the UK sites. This is thought to be a result of the different orography of the two regions and its interaction with meteorology. While southern England is flat, thus allowing a synoptic flow to be dominant at the regional scale, the Madrid Metropolitan Area lies within an air basin with a characteristic mesoscale wind circulation. Although the two rural sites are at similar distances from the main cities, Madrid and London, the rural site in the UK is only 100 m higher than the city, though in Spain it is 700 m above. All this results in a small urban influence at the Spanish rural site, whereas Harwell is strongly influenced by the regional sources that influence London. The fine nitrate in Madrid (Fig. 2a) showed a marked pattern, with small error bars, clearly dependant on temperature (linear correlation coefficient

$r = -0.90$ ). This suggests that most of the nitrate is in a thermally unstable state, most probably ammonium nitrate and thus displaced towards the gas phase at high temperatures. At the rural Campisábalos site concentrations of PM10 nitrate are much lower (Fig. 2b) than urban fine nitrate. Seasonal differences are not statistically significant. This suggests the presence of sodium or calcium, rather than ammonium, nitrates.

In the London site the lowest concentrations were also recorded in summer (Fig. 2e) and the highest values mainly in springtime from February to April. As dependence on temperature was not clear as in Madrid, other processes or source behaviour should be present. Analysing a 2002–2003 data set, Abdalmogith and Harrison (2005) found that the UK received the highest amounts of particulate nitrate and sulphate due to long range transport from central Europe during spring. This finding was recently confirmed by Baker (2010). Pollutant transport is reflected in the fine nitrate annual pattern. This type of external factor was also found by Salvador et al. (2008) who, analysing PM10 and PM2.5 filter-based SIC data from traffic, urban background and regional background monitoring sites from the Madrid airshed, showed that the Madrid air basin was also influenced by long range transport of SIC, in this case from Europe and the Western Mediterranean, in the warm season months. However, impact of long-range transport was not seen in the fine nitrate annual pattern at the Spanish sites for the study period analysed in this work.

At Harwell, fine nitrate levels (Fig. 2f) are very similar to those at Marylebone Road. Both patterns showed similarities, but Harwell displayed a more marked minimum in summer and a less

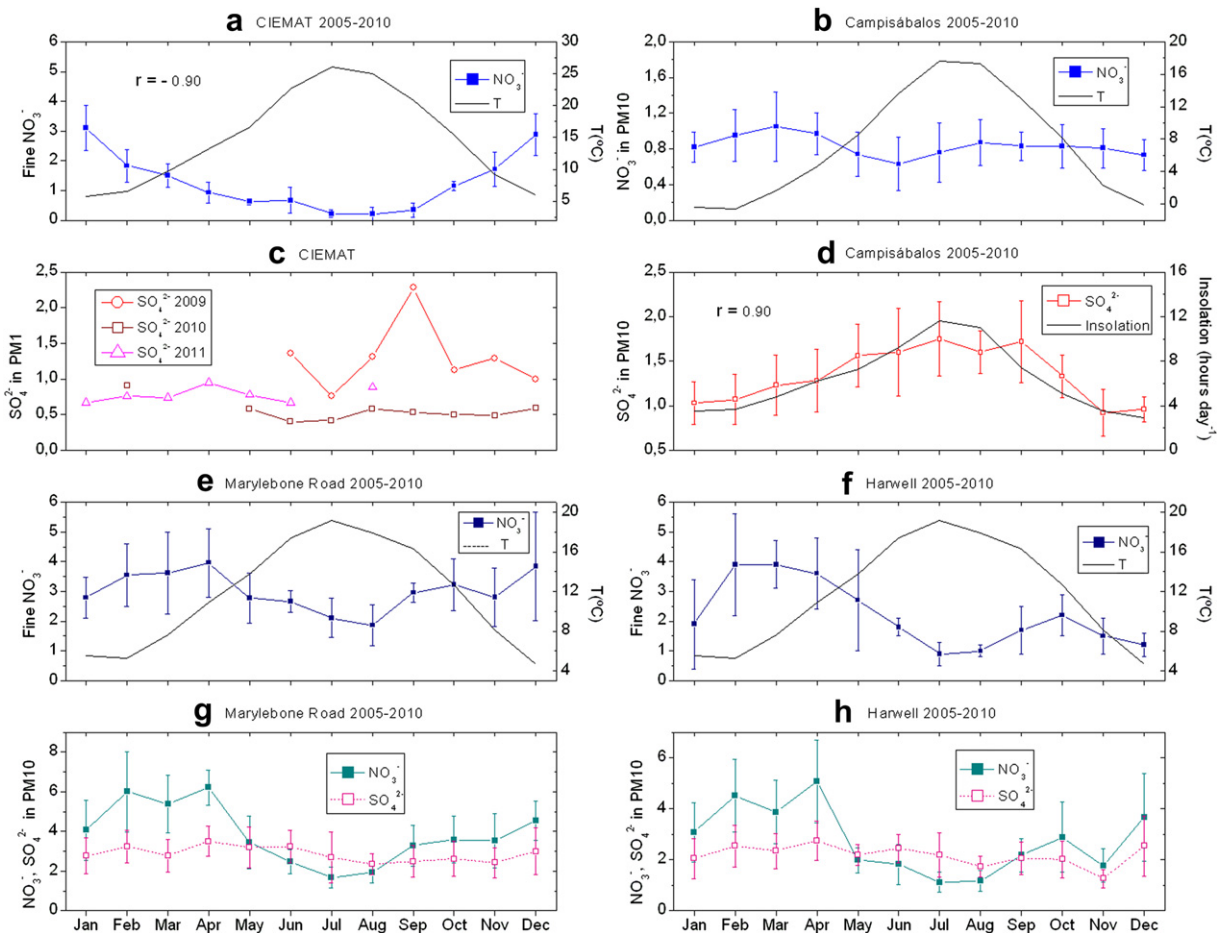


Fig. 2. Monthly average concentrations (in  $\mu\text{g m}^{-3}$ ) of nitrate and sulphate in the size fractions and time intervals indicated.



pronounced secondary maximum in autumn–winter. As Harwell is less influenced by local emissions, it is more representative of long-range transport and meteorological conditions.

PM10 nitrate (Fig. 2g and h) showed slightly higher concentrations and a similar pattern to fine nitrate at Harwell. At Marylebone Road, the Feb–Apr maximum is enhanced in PM10 nitrate. This reinforces the hypothesis of dominant locally generated ammonium nitrate in autumn and early winter and a significant contribution of transported nitrate in Feb–Apr.

PM1 sulphate in Madrid (Fig. 2c) showed a very flat pattern from 2010 on. In September 2009 concentrations were remarkably higher due to long-range transport episodes from central Europe and the Western Mediterranean (Revuelta et al., 2011). PM10 sulphate at the rural site (Fig. 2d), on the contrary, shows an insolation-dependent pattern (correlation coefficient  $r = 0.90$ ). Other researchers found higher fine sulphate concentrations in summer at urban sites in New York (Bari et al., 2003; Rattigan et al., 2006). They attributed it to the photochemical formation of sulphate from SO<sub>2</sub> through the OH radical, more effective in this season. This effect is not clearly seen in the Madrid sulphate.

Both of the UK sites present flat annual PM10 sulphate patterns (Fig. 2g and h); nevertheless, levels are higher than in the Spanish sites. The remarkable maximum seen in nitrate in springtime is not reflected in the sulphate averages. The explanation may be related to aqueous phase oxidation processes making a greater contribution to sulphate in winter in the UK context (Jones and Harrison,

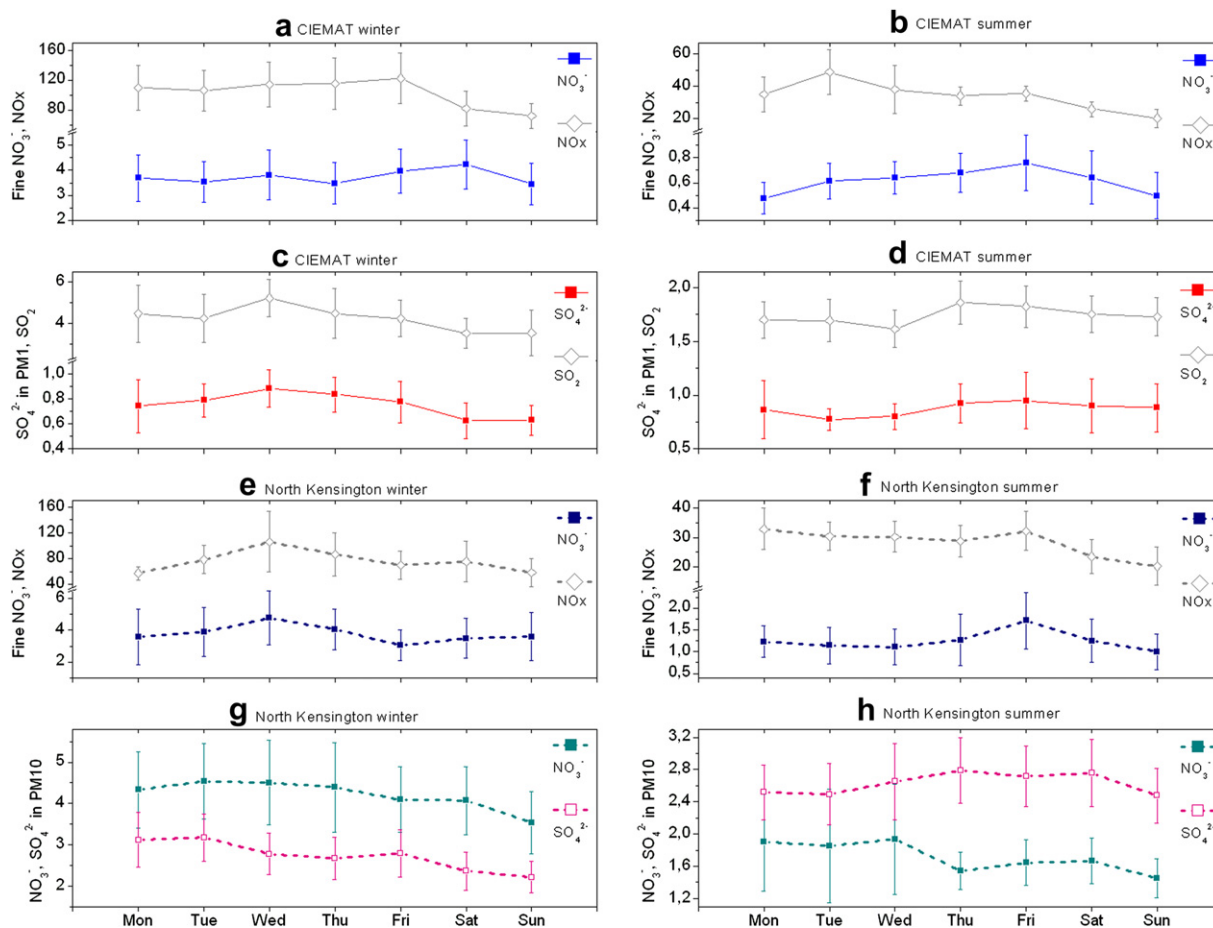
2011), and the lack of a temperature-dependent dissociation of ammonium sulphate.

### 3.2. Weekly patterns

24-Hour averages by day of the week have been computed on a seasonal basis. Fig. 3 depicts the weekly evolution of SIC and in some cases also the precursor gases NO<sub>x</sub> and SO<sub>2</sub> for the urban background sites. Winter (December–February) and summer (June–August) months have been chosen following a temperature criterion. The time periods selected for each pollutant and season have been determined by the minimum capture of 50% of data.

Fine nitrate daily averages are much lower in summer in CIEMAT than in North Kensington and similar in winter, while NO<sub>x</sub> concentrations are similar or even higher (Fig. 3a, b, e and f). This is probably a result of summer thermal decomposition of nitrate in Madrid. A pattern related to emissions is seen for NO<sub>x</sub> both in Madrid and London. Ambient concentrations are lower during the weekend, most notably in Madrid in winter. In general, nitrate evolution is related to NO<sub>x</sub> evolution, though it does not follow it closely.

Table 1 shows the particulate SIC reductions related to the weekly concentrations calculated as  $(SIC_{day} - SIC_{week})/SIC_{week}$  ( $\pm 95\%$  CI) for CIEMAT and North Kensington. Non-statistically significant reductions are not shown. In Madrid, a significant nitrate weekend reduction can be seen in summer, although the minimum



**Fig. 3.** Daily averages. (a) CIEMAT winter. Nitrate 2004/2005–2010/2011 and NO<sub>x</sub> 2009/2010–2010/2011. (b) CIEMAT summer. Nitrate 2005–2011 and NO<sub>x</sub> 2011. (c) CIEMAT winter. Sulphate and SO<sub>2</sub> 2010/2011. (d) CIEMAT summer. Sulphate and SO<sub>2</sub> 2011. (e) North Kensington winter. Nitrate and NO<sub>x</sub> 2007/2008–2008/2009. (f) North Kensington summer. Nitrate and NO<sub>x</sub> 2008–2009. (g) North Kensington winter. Nitrate and Sulphate 2004/2005–2009/2010. (h) North Kensington summer. Nitrate and Sulphate 2005–2010. Concentrations in  $\mu\text{g m}^{-3}$ .

**Table 1**  
Weekend reductions in SIC  $\pm$  95% CI.

	CIEMAT nitrate in PM2.5	CIEMAT sulphate in PM1	North K. nitrate in PM2.5	North K. sulphate in PM10
<b>Winter</b>				
Sat	–	18 $\pm$ 12%	–	–
Sun	–	16 $\pm$ 15%	–	13 $\pm$ 11%
Mon	–	–	–	–
<b>Summer</b>				
Sat	–	–	–	–
Sun	18 $\pm$ 11%	–	21 $\pm$ 16%	–
Mon	20 $\pm$ 13%	–	–	–

concentrations reached are displaced from Saturday–Sunday to Sunday–Monday, with mean reductions around 20%. In North Kensington, fine nitrate summer reductions of 21  $\pm$  16% are found on Sundays. In a similar study, Millstein et al. (2008) calculated fine nitrate variations by day of week at four US urban sites for one year. In three of these sites the authors found nitrate weekly minima on Sundays or Mondays with mean annual reductions of 21–29% related to the weekly mean. Reductions found in Madrid and London are consistent with these values. In winter, at both urban sites fine nitrate weekend reductions were not significant.

Results for SO<sub>2</sub> and sulphate at CIEMAT are depicted for winter 2010–2011 (Fig. 3c). In winter 2009–2010 meteorological conditions favoured the ventilation of the city and, with sulphate concentrations very low, no pattern was seen. In winter 2010–2011 several intense atmospheric stagnation episodes took place, favouring pollutant accumulation. Under these conditions, a regular sulphate weekly evolution appeared, with reductions above 15% for Saturdays and Sundays. This behaviour corresponds with the SO<sub>2</sub> weekend reduction. This points to urban SO<sub>2</sub> as a source for sulphate although it does not rule out a diesel primary sulphate source. Artíñano and other researchers stated that the seasonal evolution of SO<sub>2</sub> in Madrid reflected the influence of heating devices in autumn and winter, causing levels considerably higher from November to March (Artinano et al., 2003). In summer (Fig. 3d), although SO<sub>2</sub> concentrations are significantly lower than in winter, the similar sulphate concentrations reflect the great oxidising capacity and reaction rates in this season.

On 1 January 2009 the European Directive 2003/17/EC limited sulphur in all vehicle fuels to a maximum of 10 mg kg<sup>-1</sup>. These reductions were adopted earlier for some kinds of fuels in several EU countries, including Spain and the UK. Fuels for heating devices have also been refined. The installation of new facilities emitting more than 0.86 g of SO<sub>2</sub> to produce 1 kW is forbidden in Madrid. However, older devices still exist. In spite of these reductions weekly SO<sub>2</sub> and sulphate patterns demonstrate the anthropogenic influence on sulphur-derived pollutant ambient concentrations when meteorological conditions favour accumulation.

PM10 particulate SIC in winter and PM10 nitrate in summer at North Kensington show a slight weekly downward tendency (Fig. 3g and h). Significant reductions are found for sulphate on winter Sundays. Analysing data from filter-based measurements averaged between 2000 and 2002, Jones et al. (2008) did not find any SIC weekend reduction at the North Kensington or Harwell sites; nevertheless, statistical differences were found at both stations for particulate matter. In this study, a small SIC weekend reduction can be derived for the PM10 fraction, but the summer reduction for the fine nitrate is clearer.

The weekly evolution of pollutants was also investigated for Harwell, since this site might have some local anthropogenic influence (see Supplementary information). No statistically significant SIC weekend reductions were found. No weekend PM10 SIC reduction is seen at the Spanish rural site (not shown).

### 3.3. Daily patterns

Average daily SIC and precursor gas profiles have been computed seasonally from 1 h averages, separating weekdays and Sundays. Weekdays are Tuesday–Friday when a significant Monday reduction was observed.

NOx rises corresponding to the morning traffic rush hour and the secondary rush hour during the evening. In winter in Madrid, nitrate (Fig. 4a) follows closely the diurnal change in solar radiation (not shown for clarity) on weekdays. This suggests the dominance of photochemical processes in nitrate formation in Madrid, as Gómez-Moreno et al., 2007 have already stated. In summer, the morning nitrate rise started before dawn (6 UTC in average) (Fig. 4b). After 9 UTC the combined effect of the rise of the mixing height and the diurnal increase of temperature dominated over the photochemical formation of nitrate. NOx concentration is significantly lower than in winter, which can be partly explained by lower traffic emissions, but is also probably related to the greater mixing depth. The secondary evening traffic peak also appeared in nitrate in summer, but not in winter. This peak has been explained by other authors in terms of the contraction of the mixing layer (ML), which is consistent with our results, since it is hardly exhibited on Sundays, unlike the morning peak. In general, the evolution of the convective ML in the Madrid area begins 1 h after dawn, reaching the maximum value at 12–15 UTC and decreasing usually around 16 UTC (Crespi et al., 1995). Crespi et al. (1995) studied the evolution of the ML in Madrid under different synoptic conditions, obtaining a classification of meteorological scenarios. Under synoptic situations typically found in autumn and winter the ML is very shallow, not exceeding 700 m agl. In spring and summer the mixing height can be well above 2000 m agl.

In winter 2010–11 a daily PM1 sulphate pattern was found in Madrid (Fig. 4c). Both SO<sub>2</sub> and sulphate peaks are centred at noon, and concentration increased earlier in the morning on weekdays. An evening increment appeared in SO<sub>2</sub> in winter weekdays. For Sundays, the lesser data available resulted in a noisy pattern that made this increment unclear. In summer, a daily pattern with no remarkable differences between weekdays and Sundays was also seen for SO<sub>2</sub>, peaking earlier than in winter, but not for sulphate (Fig. 4d). This suggests that the increase is driven by meteorological processes rather than low-level emissions. Sulphate daily evolution differs from the results found by Wittig et al. (2004) in Pittsburgh. They found diurnal variation only in summer, consistent with local photochemical production.

To infer the source of precursor gases polar diagrams have been plotted using the OPENAIR software (Carslaw and Ropkins, 2012). Fig. 5 shows NOx and SO<sub>2</sub> concentrations at the CIEMAT site in winter as a function of wind direction and time-of-day. NOx maximum concentrations arrive in the morning from the East, while SO<sub>2</sub> arrives later in the morning and noon from the south-eastern sector. Wind directions indicate that the air masses come from the city and are a consequence of mean wind circulation in the Madrid air basin. The delay of SO<sub>2</sub> indicates that road traffic is not the main source. In North Kensington, Bigi and Harrison found a similar behaviour of SO<sub>2</sub> in both seasons. The authors suggested that the timing of the maximum was driven by the entrainment of high level emissions into the mixing layer, since polluted air from aloft is mixed downwards as the boundary layer increases in depth in the morning (Bigi and Harrison, 2010).

NOx hourly evolution is similar in both cities, though the evening increment is more marked in London. However, in North Kensington, nitrate behaviour was very different to that in CIEMAT in winter. On winter weekdays, nitrate kept steady values (Fig. 4e) with a drop in concentrations in the afternoon. In summer, the morning evolution is similar to that in Madrid, but the evening and

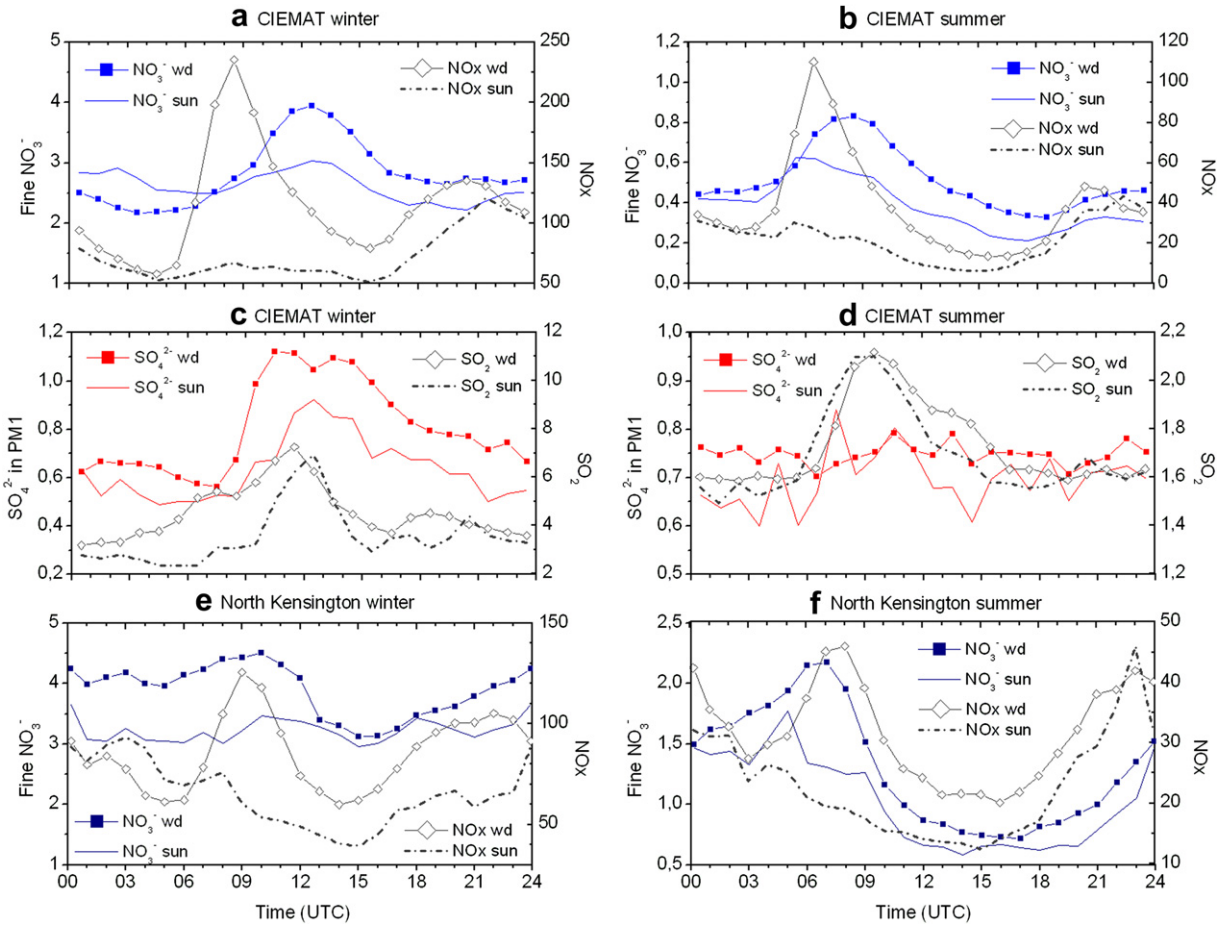


Fig. 4. Hourly averages in concentration. Time periods correspond to Fig. 3. Concentrations in  $\mu\text{g m}^{-3}$ .

night concentration rise is notably higher. The presence of the afternoon drop was detected in 2009 hourly averages in North Kensington and Harwell (Harrison et al., 2012). North Kensington fine nitrate profiles are more similar to the ones found by Wittig et al. (2004) at the Pittsburgh Supersite, located in an urban park. Nocturnal high values are explained by low temperature and high relative humidity. In Madrid, nocturnal high nitrate levels related to very high relative humidity have been observed only occasionally (Gómez-Moreno et al., 2007).

During the REPARTEE-II campaign, which took place in London in autumn 2007, Barlow et al. (2011) studied the daily evolution of the boundary layer during three weeks using a Doppler lidar. On average, they found a 800 m maximum mixing height at 13–15 h, and a delayed 600 m maximum aerosol layer height at 15–17 h. In the present work, averaged winter  $\text{NO}_x$  concentrations showed a deep minimum at 14 h on weekdays, while fine particulate nitrate showed a delayed minimum at 15–16 h on winter weekdays. The response of reactive gaseous and particulate pollutants to changes

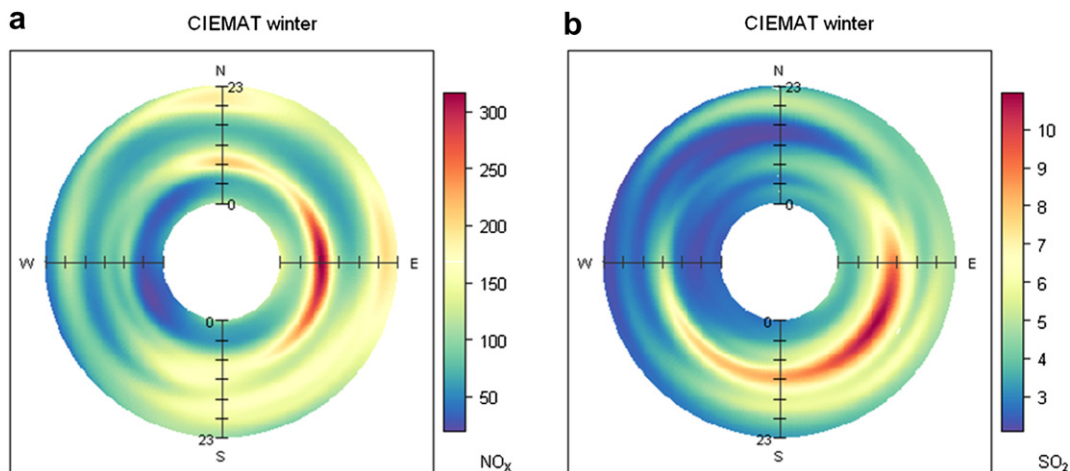


Fig. 5. Polar plots of (a)  $\text{NO}_x$  and (b)  $\text{SO}_2$  ( $\mu\text{g m}^{-3}$ ) at the CIEMAT site in winter as a function of wind direction and time-of-day. Inside of circle is 00:00–01:00 h UTC running through the day to 23:00–24:00.

in the mixing layer is not known with certainty. A different response of NOx and particulate nitrate cannot be dismissed. This result supports the hypothesis that the expansion of the mixing layer in the warmest hours of the day plays a major role in the formation of the afternoon aerosol concentration minimum.

Finally, comparing seasonally the levels reached by NOx and nitrate, it is found that hourly NOx concentrations are noticeably higher in Madrid. However, nitrate maximum hourly concentrations are higher in North Kensington, most notably in summer. The smaller seasonal difference in London can be attributed to smaller summer increments in temperature and mixing height in London (Rigby et al., 2006). This suggests, as inferred above from the weekly patterns, that nitrate formation is more efficient in London. In urban environments, nitrate in the fine fraction is mainly formed through the neutralization of gaseous nitric acid by a base, usually ammonia. A second pathway involves heterogeneous formation from NO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub> on water droplets, producing acid aerosols. Thus, the higher efficiency of nitrate formation in London could be related to ammonia availability or higher relative humidity; however, there is insufficient information on ammonia in Madrid or London to go into this topic in greater depth. Moreover, to confirm this hypothesis, pollutant apportionment between long-range transport and local formation should be quantified.

### 3.4. Ratios NO<sub>3</sub><sup>-</sup>/NOx, SO<sub>4</sub><sup>2-</sup>/SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> in Madrid

Seasonally averaged ratios of nitrate and sulphate to precursor gases and SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ratios have been calculated on a daily basis when more than 50% of data were available simultaneously (Table 2). This corresponded to one or two seasons except for the summer 2011, when only data from 1 June to 7 July were available.

Ratios of the secondary inorganic pollutants to precursor gases NO<sub>3</sub><sup>-</sup>/NOx and SO<sub>4</sub><sup>2-</sup>/SO<sub>2</sub> give some more clues about formation processes and/or aerosol sources. The gas-phase reactions responsible for the formation of particulate SIC involve the slow oxidation of SO<sub>2</sub> to sulphate and NO<sub>2</sub> to nitrate mainly by the OH radical, generated photochemically by the action of solar radiation on oxidants, and by heterogeneous processes. In principle, if photochemistry is dominant, higher oxidation ratios at summer would be expected. However, aqueous-phase reactions also generate secondary nitrate and sulphate and are more likely to take place in winter. Other processes, such as thermal decomposition of nitrate and pollutant transport can also influence the ratios.

In CIEMAT, NO<sub>3</sub><sup>-</sup>/NOx was higher in winter. In this case, it is probably a consequence of thermal decomposition, but the role of heterogeneous formation is very hard to quantify. The correlation coefficient *r* in summer was low. The small number of simultaneous NOx and nitrate data make it difficult to draw representative conclusions.

**Table 2**  
Ratios NO<sub>3</sub><sup>-</sup>/NOx, SO<sub>4</sub><sup>2-</sup>/SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup>, and correlation coefficients *r* in Madrid.

	NO <sub>3</sub> <sup>-</sup>	NOx	NO <sub>3</sub> <sup>-</sup> /NOx	<i>r</i>
Winter 2010/2011	2.60	119.24	0.03	0.74
Summer 2011	0.33	38.42	0.01	0.20
	SO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup> /SO <sub>2</sub>	<i>r</i>
Winter 2009/ 2010–2010/2011	4.32	0.88	0.29	0.31
Summer 2009	2.76	1.15	0.42	-0.13
	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup> /NO <sub>3</sub> <sup>-</sup>	<i>r</i>
Winter 2009/ 2010–2010/2011	3.59	0.87	0.71	0.40
Summer 2009–2010	0.58	0.78	1.81	0.38

The SO<sub>4</sub><sup>2-</sup>/SO<sub>2</sub> ratio was higher in summer. Sulphate levels did not show a big seasonal variation, and the ratio difference can be attributed to lower summer SO<sub>2</sub> concentrations. A small negative *r* appears in summer. This is consistent with the hypothesis of a relevant fraction of sulphate in Madrid in summer not originated from oxidation of local SO<sub>2</sub>, but being the result of a regional background with contributions from long range transport. Finally SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> was higher in summer, as a consequence of nitrate variations. Correlations were low, supporting again the hypothesis of different controlling processes for sulphate and nitrate.

## 4. Conclusions

An analysis of temporal patterns on annual, weekly and daily timescales has been performed for urban and rural sites in the central Iberian Peninsula and south-eastern UK. Patterns in precursor gases have also been considered. Results indicate the dominant processes affecting the formation and evolution of nitrate and sulphate in both regions.

NOx concentrations are higher in Madrid; nevertheless, nitrate concentrations are higher in London, most notably in summer. This might indicate that nitrate formation is more efficient in London, although thermal dissociation processes also influence nitrate concentrations. The seasonal fine nitrate pattern in Madrid was dominated by temperature-driven evolution. Concentrations at the rural site Campisábalos were comparatively very low. These factors suggest that fine nitrate in Madrid has mainly a local production origin. In contrast, the annual nitrate pattern in London shows thermal decomposition in summer, but also a notable maximum from February to April. This maximum is more clearly seen in PM10 than in PM2.5 nitrate and also at the rural UK site, Harwell, relative to the London sites which allows it to be identified with well known pollutant transport from mainland Europe.

Higher PM10 sulphate concentrations were registered in the UK. No seasonal evolution was seen though. The absence of a spring maximum attributable to European transport is surprising, but may relate to the involatility of ammonium sulphate. In Spain, photochemical formation in summer was seen at the rural site, but not in urban PM1 sulphate.

SIC weekend reductions were investigated. In both cities fine nitrate reductions around 20% are found in summer with statistical significance. These results are consistent with the findings of Millstein et al. (2008) in the US in 2008. Weekend sulphate reductions were found at the urban background sites in winter, but were only significant in Madrid.

In Madrid, the daily evolution of urban nitrate was a consequence of meteorological effects. In winter, low temperatures and the small vertical extent of the mixing layer allowed the dominance of photochemistry in nitrate formation. In summer, higher temperatures and a greater mixing height resulted in a more complex pattern. A secondary evening peak appeared in nitrate in summer. This peak has been explained in terms of the contraction of the mixing layer, which is consistent with our results, since it is not inhibited on Sundays. The pattern followed by NOx is similar in both cities; however, nitrate behaviour was very different in winter. High concentrations were registered in North Kensington at night-time, explained as a consequence of nitrate formation under high humidity conditions. Winter NOx concentration showed a deep minimum in the afternoon followed by a delayed maximum in particulate nitrate on winter weekdays in North Kensington. This behaviour is consistent with afternoon changes in the mixing layer. The results from both cities indicate that nitrate hourly evolution is predominantly determined by meteorological factors rather than by the evolution of precursor gases. For a complete interpretation of



daily pollutant evolution a complementary mixing layer study and measurement of vertical gradients is needed.

In Madrid in winter  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  peaked at noon. The same phenomenon is observed in London for  $\text{SO}_2$ , where it is explained by the entrainment of pollutants emitted at high level into the mixing layer.

$\text{SO}_4^{2-}/\text{SO}_2$  ratio in Madrid was very low, especially in summer. This is consistent with the premise that a relevant fraction of sulphate is not locally generated, but is the result of a regional background with a long range transport component.

These data analyses complement the process-based work carried out in London in the REPARTEE experiments (Harrison et al., 2012). Campaign-based measurements using both ground-based and an elevated sampling platform showed the influence of regional transport of sulphate upon sulphate concentrations in London, with concentrations aloft exceeding those at ground-level during an episode. On the other hand, nitrate fluxes were less clearly uni-directional and were much influenced by the potential of ammonium nitrate for dissociation/association (Harrison et al., 2012). The diurnal processes involved in transfer of nitrate between the condensed and vapour phases were clearly observed using single particle mass spectrometry (Dall'Osto et al., 2009) and the potential for nitrate formation via  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  was demonstrated by observations aloft on the BT Tower (ca 160 m) (Benton et al., 2010). The data analyses in this paper show strong seasonal influences, upon nitrate especially, and that behaviour seen in London is not representative of that in Madrid. The overall conclusion is therefore that the processes controlling nitrate and sulphate concentrations may vary substantially across Europe and hence observations in one city should not be assumed to be applicable elsewhere.

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## Appendix A. Supplementary information

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.atmosenv.2012.07.004>.

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