

1 COMPARISON OF TEMPORAL FEATURES OF SULPHATE AND NITRATE AT 2 URBAN AND RURAL SITES IN SPAIN AND THE UK

3 Authors: M.A. Revuelta¹, R.M. Harrison^{2,3}, L. Núñez¹, F.J. Gomez-Moreno¹, M. Pujadas¹ and
4 B. Artíñano¹

5 ¹ Environmental Department. CIEMAT. Avda. Complutense 40, Madrid, 28040, Spain

6 ² School of Geography, Earth & Environmental Sciences. Division of Environmental Health &
7 Risk Management. University of Birmingham, Edgbaston, Birmingham, B15 2TT, United
8 Kingdom

9 ³ Department of Environmental Sciences / Center of Excellence in Environmental Studies,
10 King Abdulaziz University, Jeddah, 21589, Saudi Arabia

11

12 Abstract

13 A seasonal comparison of aerosol secondary inorganic component (SIC) patterns on annual,
14 weekly and daily timescales has been performed at urban Madrid and London and at rural
15 sites in the central Iberian Peninsula and south-eastern UK alongside data for precursor gases.
16 A database from winter 2004 to summer 2011 has been analysed. Results show the dominant
17 processes affecting the formation and evolution of nitrate (NO_3^-) and sulphate (SO_4^{2-}) in both
18 regions. In Madrid, photochemistry dominates formation of nitrate, which is mostly locally-
19 generated. Strong thermal decomposition results in very low concentrations in summer. In
20 contrast, in London high nocturnal values suggest the importance of heterogeneous formation
21 processes as well as nitrate condensation at lower temperatures. The seasonal nitrate
22 maximum in the UK is found in late winter-early spring, when the region typically receives
23 the highest input of pollutants transported from mainland Europe. Daily evolution of nitrate in
24 both cities is heavily influenced by meteorological factors. Seasonal sulphate patterns show no
25 obvious trend, except at the Spanish rural site in summer where photochemical formation was
26 apparent. In Madrid, daily SO_2 and sulphate patterns exhibiting maximum concentrations at
27 noon were found in winter. In previous studies this phenomenon was observed for SO_2 in
28 London, where it was explained by the entrainment of pollutants from aloft into the mixing
29 layer. SIC weekend reductions were investigated at the urban background sites of Madrid and
30 London, and in both cities statistically significant fine nitrate reductions of around 20% are
31 found in summer. These values are consistent with the annual reductions observed by
32 researchers in the US. Weekend sulphate reductions occurred in winter, reflecting a clear
33 impact of anthropogenic sulphate in urban environments, in spite of the large reductions in
34 sulphur emissions in Europe in the last decade. Ratios of nitrate and sulphate to oxidant gases
35 and to one another have been calculated for Madrid, and are consistent with a contribution of

36local formation to sulphate in winter, while in summer a regional background unrelated to
37urban SO₂ is observed. The strong differences in the behaviour seen in London and Madrid
38(and the rural sites) emphasises the need to study cities individually and not to extrapolate
39conclusions drawn in one city to others in different climate/topographic situations.

40

411-Introduction

42Secondary inorganic aerosol is the result of transformation processes of primary pollutants in
43the atmosphere which depend on emissions as well as on meteorology. Such pollutants can be
44transported from the source region to thousands of km away, which means that an
45interpretation of aerosol behaviour in a zone not only requires information on sources and
46pathways in that region but also on pollutants transported from other source areas.

47Both meteorology and emissions show large differences in different regions of Europe, and
48conclusions from a certain region cannot be extrapolated to other parts of the continent. A
49compendium of European aerosol phenomenology including chemical characteristics of
50particulate matter at kerbside, urban, rural and background sites is presented in Putaud et al
51(2004) and Putaud et al (2010). Querol et al (2004) analysed PM characteristics of seven
52European regions comparing levels and speciation studies of PM₁₀ and PM_{2.5}. They found in
53Central Europe (including UK) annual mean values of SIC slightly higher than those found in
54Southern Europe, where the difference between rural and urban sites was larger. It was
55noticeable that SIC levels were very similar in all urban areas, with an extra input in
56intensively industrialised regions or heavily polluted urban areas. Regarding long-range
57transport, Borge et al (2007) found very different and characteristic transport patterns that
58affected PM₁₀ concentrations in three European cities: Athens, Madrid and Birmingham.

59The joint analysis of pollutant and meteorological data on different timescales provides
60information on the dominant processes that govern aerosol formation and transport.
61Competing effects lead to different patterns in different locations. Nitrate in the fine fraction,
62mainly ammonium nitrate, is partitioned into a gaseous and a particulate phase, this partition
63depending on temperature. As sulphate and coarse nitrate are more thermally and chemically
64stable, they are more affected by transport processes, whereas fine nitrate evolution is
65expected to be more affected by local meteorology and formation/dissociation processes.

66Time evolution of pollutants on a yearly timescale reveals a seasonal pattern related to
67emissions and climate. Weekday/weekend analysis provides information on the formation and
68accumulation time of secondary pollutants in the atmosphere, but moreover, since there is no
69natural process which follows a seven day cycle, it can provide information on the
70anthropogenic influence on a certain site. The daily pattern not only gives us information

71 about the origin of pollutants, since a marked anthropogenic emission pattern indicates
72 anthropogenic local/regional provenance, but also on the formation processes involved. In the
73 last decade, several researchers have analysed aerosol behaviour on different timescales.
74 Rattigan et al (2006) reported fine nitrate and sulphate seasonal patterns in a rural and an
75 urban site in the state of New York, finding maximum sulphate concentrations in the warmer
76 months, and highest nitrate in the colder periods. They concluded that photochemistry was the
77 dominant formation mechanism for sulphate aerosol, while nitrate concentration was driven
78 by thermal dissociation of ammonium nitrate. Millstein et al (2008) investigated the fine
79 particle nitrate response to weekly changes in emissions at four US urban sites. They found a
80 reduction in measured concentrations of PM nitrate on weekends associated with lower NO_x
81 emissions, indicating the potential to reduce PM_{2.5} nitrate via NO_x control. Recently,
82 Bampardimos et al (2011) investigated the weekly cycle of coarse and fine mode PM in
83 different types of rural and urban stations in Switzerland to calculate the contribution of traffic
84 to the coarse mode urban ambient concentrations. Wittig et al (2004) studied diurnal patterns
85 of nitrate and sulphate on a seasonal base at the Pittsburgh Supersite, relating features of the
86 patterns to temperature, RH, and ultraviolet radiation that affected the formation processes of
87 secondary aerosol.

88 In this paper we perform a comparison of the temporal features of nitrate and sulphate in the
89 south-eastern UK and the central part of the Iberian Peninsula. Results from five sites,
90 including urban background sites in the two capitals, Madrid and London, and nearby rural
91 sites are presented. This study aims to elucidate the processes that dominate the formation and
92 evolution of SIC in winter and summer in the two European cities.

93

94 **2-Sampling sites and techniques**

95 **2.1-Meteorology and topography**

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

105The geography of south-eastern England consists of lowland terrain, with heights not
106exceeding 400 m. The main meteorological influence is the proximity to the Atlantic Ocean,
107which results in a humid and windy maritime climate, subject to frequent changes.

108Climatic information can be obtained from the meteorological services of both countries
109(<http://www.aemet.es/es/serviciosclimaticos> and <http://www.metoffice.gov.uk/climate/uk/>).

110Seasonal comparison of relevant meteorological parameters averaged from 1971 to 2000
111shows important differences that are likely to influence aerosol formation and transformation.
112Mean temperatures are higher in Madrid than London, but the difference is larger in summer
113(6-8 °C in Madrid and 4-5 °C in London in winter; 20-25 °C Madrid and around 17°C London
114in summer). However, sunshine and precipitation make the largest differences. Sunshine in
115winter is around 425 hours in Madrid and 170 in London, while in summer it reaches 1 000
116hours in Madrid and 600 in London. On the other hand, average rainfall is 130 mm in winter
117and only 30 mm in summer in Madrid, while precipitation in southern England is over 200
118mm in both seasons.

119Since the Spanish rural site is significantly elevated above the level of the city (see Fig. 1),
120meteorological features are different. The wind regime is affected by the mountainous
121topography. Temperatures are lower and mean precipitation is higher. In contrast, climatic
122differences between the UK sites are small.

1232.2-Spain sites and measurements

124The metropolitan area of Madrid has more than 6 million inhabitants and more than 2.5
125million residents live in the surrounding towns. It comprises a car fleet over 4 million vehicles
126(fifty percent of which are diesel powered, including more than six hundred thousand
127medium- and heavy-duty trucks) with very intense traffic on weekdays on the connecting
128radial roads and the several existing ring roads. Emissions from light industry and domestic
129heating in winter contribute to a lesser extent. Gas boilers are the predominant domestic
130heating devices, while fuel-oil and coal boilers are also present but in a much lower
131percentage. These features, together with the long distance between the Madrid metropolitan
132area and other significant urban or industrial areas in central Spain (around 200 km), allow
133study of local influences.

134One of the sampling sites was located within the CIEMAT facilities in the north western area
135of the city of Madrid (40° 27.5'N, 3° 43.5'W, 669 m asl). This site is representative of urban
136background conditions. It is located in the north-west section of the city, close to the outskirts
137of the city in an area largely covered by vegetation but with some heavily trafficked roads
138(none close to the sampler).

139Gaseous pollutants, particulate SIC concentrations and meteorological parameters were
140continuously recorded.

141The rural site selected for this study is Campisábalos, a regional background monitoring site
142included in the air quality network of the **European Monitoring and Evaluation Programme**
143(EMEP). This site is located in the center of the Iberian Peninsula (41° 17' N, 3° 09' W, 1 360
144m asl), on the far north-eastern limit of the Madrid air basin and 100 km away from the city. It
145is surrounded mainly by coniferous forest and in a small proportion by farmland and pasture.
146PM10 filters are collected daily and analysed for ions. Temperature and insolation data were
147collected from the Spanish Meteorological Service (AEMET) station in Puerto de
148Navacerrada (40° 46.83' N, 4° 0.62', 1 894 m asl).

149Figure 1

1502.3-UK sites and measurements

151UK data have been obtained for sites that form part of the UK Automatic Urban and Rural
152Network (AURN) and the London Network.

153With a population over 7 million inhabitants, London is by far the largest city in the UK.

154The Marylebone Road monitoring station (51° 32.6' N, 0° 9.92' W, 27 m asl) is one of the
155sites selected for this study. It is located on the kerbside of a major arterial route within the
156City of Westminster in London. Traffic flows of over 80 000 vehicles per day pass the site on
1576 lanes with frequent congestion.

158North Kensington (51° 31.27' N, 0° 12.8' W) is an urban background site located in a
159residential area to the west of central London, approximately 4 km from the Marylebone Road
160site. The nearest road is approximately 30 metres from the station with an average daily traffic
161flow of 8 000 vehicles per day. There are a number of retail and light industrial units located
162within the vicinity to the east and west of the monitoring station.

163The Harwell rural site (51° 34.72' N, 1° 20.26' W, 137 m asl) is also an EMEP site and is
164located within the grounds of the Harwell Science Centre, in the middle of an unfarmed field
165and surrounded by predominantly agricultural land. It is around 85 km from London. There is
166limited activity in the area. Distant sources include the busy A34 dual carriageway about 2 km
167to the east and the Didcot power station about 5 km to the north-east. A careful analysis of the
168influence of the power station has shown that it accounts for only 3.3% of the annual mean
169sulphur dioxide measured at Harwell (Jones and Harrison 2011).

170These sites are equipped with continuous monitors recording fine nitrate concentration and
171gases. PM10 filters are collected daily and analysed for ions.

1722.4 – Techniques

173Spain: Fine nitrate concentration was measured using a Rupprecht and Patashnick 8400N
174Nitrate Analyser with a PM2.5 sampling inlet (Long et al, 2006) on a 10-min time basis.

175Semicontinuous PM1 sulphate concentration was registered with a Thermo 5020 sulfate
176particulate analyzer (SPA) (Schwab et al, 2006) on a time basis of 20 minutes. Both
177instruments were successfully compared to filter-based measurements. Gaseous species (SO₂,
178NO and NO₂) at the CIEMAT site were measured by a DOAS spectrometer (OPSIS AR-500)
179along a 228 m horizontal path with a mean height of 10 m above ground. The measurement
180frequency was similar to the particulate nitrate instrument. Meteorological information was
181obtained from a permanent tower installed at CIEMAT with temperature at 4 m. Data were
182recorded every 10 min. At Campisábalos, PM10 filters are collected with an Andersen
183GUV15H, and particulate sulfate and nitrate concentrations are determined by Ion
184Chromatography (IC).

185U.K.: Fine nitrate concentration was measured using a Rupprecht and Patashnick 8400N
186Nitrate Analyser with a PM2.5 sampling inlet. Gaseous nitrogen oxides in the UK sites are
187measured hourly using the chemiluminescence technique. Gaseous SO₂ is measured by UV
188fluorescence. Filters at UK sites are collected using a Partisol sampler with a PM10 inlet and
189analysed for ions by IC. Meteorological data in the UK have been obtained from London
190Heathrow (51° 28.74' N, 0° 26.94' W, 25 m asl) which lies between the London sites and
191Harwell.

192All plots use UTC time and averages have been computed if 50% of the data was captured
193over the averaging interval. Error bars are based on 95% confidence intervals (CI) of the
194mean.

195

1963-Results

1973.1-Annual patterns

198Monthly averages have been computed to obtain a seasonal pattern for nitrate and sulphate in
199four sampling sites. Six years of data (2005 to 2010) have been computed except for the
200sulphate in Madrid, where available data started in June 2009. Due to this fact and the
201significant differences found in these three years, measurement periods were plotted
202separately. In London, the site selected to calculate the seasonal evolution is Marylebone Road
203due to the higher data availability. A comparison with the urban background site did not show
204significant differences in the nitrate and sulphate monthly means (see Supplementary
205Information for North Kensington).

206Figure 2

207In central Spain, the highest nitrate monthly means are around $3 \mu\text{g m}^{-3}$ at the urban
208background site and three times lower at the rural site. The sulphate concentrations show
209smaller differences, being below $2.5 \mu\text{g m}^{-3}$. In London and also at the rural Harwell site the
210fine nitrate monthly means are above the Madrid concentrations, reaching $4 \mu\text{g m}^{-3}$. PM10
211nitrate and sulphate concentrations in Harwell are smaller than in London, but well above
212Campisábalos.

213The behaviour of pollutants at both Spanish sites is very different, unlike the UK sites. This is
214thought to be a result of the different orography of the two regions and its interaction with
215meteorology. While southern England is flat, thus allowing a synoptic flow to be dominant at
216the regional scale, the Madrid Metropolitan Area lies within an air basin with a characteristic
217mesoscale wind circulation. Although the two rural sites are at similar distances from the main
218cities, Madrid and London, the rural site in the UK is only 100 m higher than the city, though
219in Spain it is 700 m above. All this results in a small urban influence at the Spanish rural site,
220whereas Harwell is strongly influenced by the regional sources that influence London. The
221fine nitrate in Madrid (Fig 2a) showed a marked pattern, with small error bars, clearly
222dependant on temperature (linear correlation coefficient $r = -0.90$). This suggests that most of
223the nitrate is in a thermally unstable state, most probably ammonium nitrate and thus displaced
224towards the gas phase at high temperatures. At the rural Campisábalos site concentrations of
225PM10 nitrate are much lower (Fig 2b) than urban fine nitrate. Seasonal differences are not
226statistically significant. This suggests the presence of sodium or calcium, rather than
227ammonium, nitrates.

228In the London site the lowest concentrations were also recorded in summer (Fig 2e) and the
229highest values mainly in springtime from February to April. As dependence on temperature
230was not as clear as in Madrid, other processes or source behaviour should be present.
231Analysing a 2002-2003 data set, Abdalmogith and Harrison (2005) found that the UK
232received the highest amounts of particulate nitrate and sulphate due to long range transport
233from central Europe during spring. This finding was recently confirmed by Baker (2010).
234Pollutant transport is reflected in the fine nitrate annual pattern. This type of external factor
235was also found by Salvador et al (2008) who, analysing PM10 and PM2.5 filter-based SIC
236data from traffic, urban background and regional background monitoring sites from the
237Madrid airshed, showed that the Madrid air basin was also influenced by long range transport
238of SIC, in this case from Europe and the Western Mediterranean, in the warm season months.
239However, impact of long-range transport was not seen in the fine nitrate annual pattern at the
240Spanish sites for the study period analysed in this work.

241At Harwell, fine nitrate levels (Fig 2f) are very similar to those at Marylebone Road. Both
242patterns showed similarities, but Harwell displayed a more marked minimum in summer and a
243less pronounced secondary maximum in autumn-winter. As Harwell is less influenced by local
244emissions, it is more representative of long-range transport and meteorological conditions.

245PM10 nitrate (Fig 2g, 2h) showed slightly higher concentrations and a similar pattern to fine
246nitrate at Harwell. At Marylebone Road, the Feb-Apr maximum is enhanced in PM10 nitrate.
247This reinforces the hypothesis of dominant locally generated ammonium nitrate in autumn and
248early winter and a significant contribution of transported nitrate in Feb-Apr.

249PM1 sulphate in Madrid (Fig 2c) showed a very flat pattern from 2010 on. In September 2009
250concentrations were remarkably higher due to long-range transport episodes from central
251Europe and the Western Mediterranean (Revuelta et al, 2011). PM10 sulphate at the rural site
252(Fig 2d), on the contrary, shows an insolation-dependent pattern (correlation coefficient r
253=0.90). Other researchers found higher fine sulphate concentrations in summer at urban sites
254in New York (Bari et al, 2003; Rattigan et al, 2006). They attributed it to the photochemical
255formation of sulphate from SO₂ through the OH radical, more effective in this season. This
256effect is not clearly seen in the Madrid sulphate.

257Both of the UK sites present flat annual PM10 sulphate patterns (Fig 2g, 2h); nevertheless,
258levels are higher than in the Spanish sites. The remarkable maximum seen in nitrate in
259springtime is not reflected in the sulphate averages. The explanation may be related to
260aqueous phase oxidation processes making a greater contribution to sulphate in winter in the
261UK context (Jones and Harrison, 2011), and the lack of a temperature-dependent dissociation
262of ammonium sulphate.

2633.2-Weekly patterns

26424-Hour averages by day of the week have been computed on a seasonal basis. Figure 3 depicts
265the weekly evolution of SIC and in some cases also the precursor gases NO_x and SO₂ for the
266urban background sites. Winter (December to February) and summer (June to August) months
267have been chosen following a temperature criterion. The time periods selected for each
268pollutant and season have been determined by the minimum capture of 50% of data.

269Figure 3

270Fine nitrate daily averages are much lower in summer in CIEMAT than in North Kensington
271and similar in winter, while NO_x concentrations are similar or even higher (Fig. 3a, 3b, 3e and
2723f). This is probably a result of summer thermal decomposition of nitrate in Madrid. A pattern
273related to emissions is seen for NO_x both in Madrid and London. Ambient concentrations are
274lower during the weekend, most notably in Madrid in winter. In general, nitrate evolution is
275related to NO_x evolution, though it does not follow it closely.

276 Table I shows the particulate SIC reductions related to the weekly concentrations calculated as
277 $(SIC_{day} - SIC_{week}) / SIC_{week}$ (\pm 95% CI) for CIEMAT and North Kensington. Non-statistically
278 significant reductions are not shown. In Madrid, a significant nitrate weekend reduction can be
279 seen in summer, although the minimum concentrations reached are displaced from Saturday-
280 Sunday to Sunday-Monday, with mean reductions around 20%. In North Kensington, fine
281 nitrate summer reductions of 21 ± 16 % are found on Sundays. In a similar study, Millstein et
282 al. (2008) calculated fine nitrate variations by day of week at four US urban sites for one year.
283 In three of these sites the authors found nitrate weekly minima on Sundays or Mondays with
284 mean annual reductions of 21-29% related to the weekly mean. Reductions found in Madrid
285 and London are consistent with these values. In winter, at both urban sites fine nitrate
286 weekend reductions were not significant.

287 Table I

288 Results for SO₂ and sulphate at CIEMAT are depicted for winter 2010-2011 (Fig 3c). In
289 winter 2009-2010 meteorological conditions favoured the ventilation of the city and, with
290 sulphate concentrations very low, no pattern was seen. In winter 2010-2011 several intense
291 atmospheric stagnation episodes took place, favouring pollutant accumulation. Under these
292 conditions, a regular sulphate weekly evolution appeared, with reductions above 15% for
293 Saturdays and Sundays. This behaviour corresponds with the SO₂ weekend reduction. This
294 points to urban SO₂ as a source for sulphate although it does not rule out a diesel primary
295 sulphate source. Artíñano and other researchers stated that the seasonal evolution of SO₂ in
296 Madrid reflected the influence of heating devices in autumn and winter, causing levels
297 considerably higher from November to March (Artíñano et al, 2003). In summer (Fig 3d),
298 although SO₂ concentrations are significantly lower than in winter, the similar sulphate
299 concentrations reflect the great oxidising capacity and reaction rates in this season.

300 On 1 January 2009 the European Directive 2003/17/EC limited sulphur in all vehicle fuels to a
301 maximum of 10 mg kg⁻¹. These reductions were adopted earlier for some kinds of fuels in
302 several EU countries, including Spain and the UK. Fuels for heating devices have also been
303 refined. The installation of new facilities emitting more than 0.86 g of SO₂ to produce 1kW is
304 forbidden in Madrid. However, older devices still exist. In spite of these reductions weekly
305 SO₂ and sulphate patterns demonstrate the anthropogenic influence on sulphur-derived
306 pollutant ambient concentrations when meteorological conditions favour accumulation.

307 PM₁₀ particulate SIC in winter and PM₁₀ nitrate in summer at North Kensington show a
308 slight weekly downward tendency (Fig 3g, 3h). Significant reductions are found for sulphate
309 on winter Sundays. Analysing data from filter-based measurements averaged between 2000
310 and 2002, Jones et al (2008) did not find any SIC weekend reduction at the North Kensington

311or Harwell sites; nevertheless, statistical differences were found at both stations for particulate
312matter. In this study, a small SIC weekend reduction can be derived for the PM10 fraction, but
313the summer reduction for the fine nitrate is clearer.

314The weekly evolution of pollutants was also investigated for Harwell, since this site might
315have some local anthropogenic influence (see Supplementary Information). No statistically
316significant SIC weekend reductions were found. No weekend PM10 SIC reduction is seen at
317the Spanish rural site (not shown).

3183.3-Daily patterns

319Average daily SIC and precursor gas profiles have been computed seasonally from 1h
320averages, separating weekdays and Sundays. Weekdays are Tuesday to Friday when a
321significant Monday reduction was observed.

322Figure 4

323NO_x rises corresponding to the morning traffic rush hour and the secondary rush hour during
324the evening. In winter in Madrid, nitrate (Fig 4a) follows closely the diurnal change in solar
325radiation (not shown for clarity) on weekdays. This suggests the dominance of photochemical
326processes in nitrate formation in Madrid, as Gomez-Moreno et al (2007) have already stated.
327In summer, the morning nitrate rise started before dawn (6 UTC in average) (Fig 4b). After 9
328UTC the combined effect of the rise of the mixing height and the diurnal increase of
329temperature dominated over the photochemical formation of nitrate. NO_x concentration is
330significantly lower than in winter, which can be partly explained by lower traffic emissions,
331but is also probably related to the greater mixing depth. The secondary evening traffic peak
332also appeared in nitrate in summer, but not in winter. This peak has been explained by other
333authors in terms of the contraction of the mixing layer (ML), which is consistent with our
334results, since it is hardly exhibited on Sundays, unlike the morning peak. In general, the
335evolution of the convective ML in the Madrid area begins 1h after dawn, reaching the
336maximum value at 12-15 UTC and decreasing usually around 16 UTC (Crespí et al, 1995).
337Crespí et al (1995) studied the evolution of the ML in Madrid under different synoptic
338conditions, obtaining a classification of meteorological scenarios. Under synoptic situations
339typically found in autumn and winter the ML is very shallow, not exceeding 700 m agl. In
340spring and summer the mixing height can be well above 2 000 m agl.

341In winter 2010-11 a daily PM1 sulphate pattern was found in Madrid (Fig 4c). Both SO₂ and
342sulphate peaks are centred at noon, and concentration increased earlier in the morning on
343weekdays. An evening increment appeared in SO₂ in winter weekdays. For Sundays, the lesser
344data available resulted in a noisy pattern that made this increment unclear. In summer, a daily
345pattern with no remarkable differences between weekdays and Sundays was also seen for SO₂,

346peaking earlier than in winter, but not for sulphate (Fig 4d). This suggests that the increase is
347driven by meteorological processes rather than low-level emissions. Sulphate daily evolution
348differs from the results found by Wittig et al (2004) in Pittsburgh. They found diurnal
349variation only in summer, consistent with local photochemical production.

350To infer the source of precursor gases polar diagrams have been plotted using the OPENAIR
351software (Carslaw et al, 2011). Figure 5 shows NO_x and SO₂ concentrations at the CIEMAT
352site in winter as a function of wind direction and time-of-day. NO_x maximum concentrations
353arrive in the morning from the East, while SO₂ arrives later in the morning and noon from the
354south-eastern sector. Wind directions indicate that the air masses come from the city and are a
355consequence of mean wind circulation in the Madrid air basin. The delay of SO₂ indicates that
356road traffic is not the main source. In North Kensington, Bigi and Harrison found a similar
357behaviour of SO₂ in both seasons. The authors suggested that the timing of the maximum was
358driven by the entrainment of high level emissions into the mixing layer, since polluted air
359from aloft is mixed downwards as the boundary layer increases in depth in the morning (Bigi
360and Harrison, 2010).

361Figure 5

362NO_x hourly evolution is similar in both cities, though the evening increment is more marked
363in London. However, in North Kensington, nitrate behaviour was very different to that in
364CIEMAT in winter. On winter weekdays, nitrate kept steady values (Fig 4e) with a drop in
365concentrations in the afternoon. In summer, the morning evolution is similar to that in Madrid,
366but the evening and night concentration rise is notably higher. The presence of the afternoon
367drop was detected in 2009 hourly averages in North Kensington and Harwell (Harrison et al,
3682012a). North Kensington fine nitrate profiles are more similar to the ones found by Wittig et
369al (2004) at the Pittsburgh Supersite, located in an urban park. Nocturnal high values are
370explained by low temperature and high relative humidity. In Madrid, nocturnal high nitrate
371levels related to very high relative humidity have been observed only occasionally (Gomez-
372Moreno et al, 2007).

373During the REPARTEE-II campaign, which took place in London in autumn 2007, Barlow et
374al (2011) studied the daily evolution of the boundary layer during three weeks using a Doppler
375lidar. On average, they found a 800 m maximum mixing height at 13-15 h, and a delayed 600
376m maximum aerosol layer height at 15-17 h. In the present work, averaged winter NO_x
377concentrations showed a deep minimum at 14h on weekdays, while fine particulate nitrate
378showed a delayed minimum at 15-16h on winter weekdays. The response of reactive gaseous
379and particulate pollutants to changes in the mixing layer is not known with certainty. A
380different response of NO_x and particulate nitrate cannot be dismissed. This result supports the

381hypothesis that the expansion of the mixing layer in the warmest hours of the day plays a
382major role in the formation of the afternoon aerosol concentration minimum.

383Finally, comparing seasonally the levels reached by NO_x and nitrate, it is found that hourly
384NO_x concentrations are noticeably higher in Madrid. However, nitrate maximum hourly
385concentrations are higher in North Kensington, most notably in summer. The smaller seasonal
386difference in London can be attributed to smaller summer increments in temperature and
387mixing height in London (Rigby et al, 2006). This suggests, as inferred above from the weekly
388patterns, that nitrate formation is more efficient in London. In urban environments, nitrate in
389the fine fraction is mainly formed through the neutralization of gaseous nitric acid by a base,
390usually ammonia. A second pathway involves heterogeneous formation from NO₃ or N₂O₅ on
391water droplets, producing acid aerosols. Thus, the higher efficiency of nitrate formation in
392London could be related to ammonia availability or higher relative humidity; however, there is
393insufficient information on ammonia in Madrid or London to go into this topic in greater
394depth. Moreover, to confirm this hypothesis, pollutant apportionment between long-range
395transport and local formation should be quantified.

396**3.4-Ratios NO₃⁻/NO_x, SO₄²⁻/SO₂ and SO₄²⁻/NO₃⁻ in Madrid**

397Seasonally averaged ratios of nitrate and sulphate to precursor gases and SO₄²⁻/NO₃⁻ ratios
398have been calculated on a daily basis when more than 50% of data were available
399simultaneously (Table II). This corresponded to one or two seasons except for the summer
4002011, when only data from 1 June to 7 July were available.

401Table II

402Ratios of the secondary inorganic pollutants to precursor gases NO₃⁻/NO_x and SO₄²⁻/SO₂ give
403some more clues about formation processes and/or aerosol sources. The gas-phase reactions
404responsible for the formation of particulate SIC involve the slow oxidation of SO₂ to sulphate
405and NO₂ to nitrate mainly by the OH radical, generated photochemically by the action of solar
406radiation on oxidants, and by heterogeneous processes. In principle, if photochemistry is
407dominant, higher oxidation ratios at summer would be expected. However, aqueous-phase
408reactions also generate secondary nitrate and sulphate and are more likely to take place in
409winter. Other processes, such as thermal decomposition of nitrate and pollutant transport can
410also influence the ratios.

411In CIEMAT, NO₃⁻/NO_x was higher in winter. In this case, it is probably a consequence of
412thermal decomposition, but the role of heterogeneous formation is very hard to quantify. The
413correlation coefficient *r* in summer was low. The small number of simultaneous NO_x and
414nitrate data make it difficult to draw representative conclusions.

415The $\text{SO}_4^{2-}/\text{SO}_2$ ratio was higher in summer. Sulphate levels did not show a big seasonal
416variation, and the ratio difference can be attributed to lower summer SO_2 concentrations. A
417small negative r appears in summer. This is consistent with the hypothesis of a relevant
418fraction of sulphate in Madrid in summer not originated from oxidation of local SO_2 , but being
419the result of a regional background with contributions from long range transport. Finally
420 $\text{SO}_4^{2-}/\text{NO}_3^-$ was higher in summer, as a consequence of nitrate variations. Correlations were
421low, supporting again the hypothesis of different controlling processes for sulphate and
422nitrate.

423

4244-**Conclusions**

425An analysis of temporal patterns on annual, weekly and daily timescales has been performed
426for urban and rural sites in the central Iberian Peninsula and south-eastern UK. Patterns in
427precursor gases have also been considered. Results indicate the dominant processes affecting
428the formation and evolution of nitrate and sulphate in both regions.

429 NO_x concentrations are higher in Madrid; nevertheless, nitrate concentrations are higher in
430London, most notably in summer. This might indicate that nitrate formation is more efficient
431in London, although thermal dissociation processes also influence nitrate concentrations. The
432seasonal fine nitrate pattern in Madrid was dominated by temperature-driven evolution.
433Concentrations at the rural site Campisábalos were comparatively very low. These factors
434suggest that fine nitrate in Madrid has mainly a local production origin. In contrast, the annual
435nitrate pattern in London shows thermal decomposition in summer, but also a notable
436maximum from February to April. This maximum is more clearly seen in PM_{10} than in
437 $\text{PM}_{2.5}$ nitrate and also at the rural UK site, Harwell, relative to the London sites which allows
438it to be identified with well known pollutant transport from mainland Europe.

439Higher PM_{10} sulphate concentrations were registered in the UK. No seasonal evolution was
440seen though. The absence of a spring maximum attributable to European transport is
441surprising, but may relate to the involatility of ammonium sulphate. In Spain, photochemical
442formation in summer was seen at the rural site, but not in urban PM_{10} sulphate.

443SIC weekend reductions were investigated. In both cities fine nitrate reductions around 20%
444are found in summer with statistical significance. These results are consistent with the
445findings of Millstein et al (2008) in the US in 2008. Weekend sulphate reductions were found
446at the urban background sites in winter, but were only significant in Madrid.

447In Madrid, the daily evolution of urban nitrate was a consequence of meteorological effects. In
448winter, low temperatures and the small vertical extent of the mixing layer allowed the
449dominance of photochemistry in nitrate formation. In summer, higher temperatures and a

450 greater mixing height resulted in a more complex pattern. A secondary evening peak appeared
451 in nitrate in summer. This peak has been explained in terms of the contraction of the mixing
452 layer, which is consistent with our results, since it is not inhibited on Sundays. The pattern
453 followed by NO_x is similar in both cities; however, nitrate behaviour was very different in
454 winter. High concentrations were registered in North Kensington at night-time, explained as a
455 consequence of nitrate formation under high humidity conditions. Winter NO_x concentration
456 showed a deep minimum in the afternoon followed by a delayed maximum in particulate
457 nitrate on winter weekdays in North Kensington. This behaviour is consistent with afternoon
458 changes in the mixing layer. The results from both cities indicate that nitrate hourly evolution
459 is predominantly determined by meteorological factors rather than by the evolution of
460 precursor gases. For a complete interpretation of daily pollutant evolution a complementary
461 mixing layer study and measurement of vertical gradients is needed.

462 In Madrid in winter SO₂ and SO₄²⁻ peaked at noon. The same phenomenon is observed in
463 London for SO₂, where it is explained by the entrainment of pollutants emitted at high level
464 into the mixing layer.

465 SO₄²⁻/SO₂ ratio in Madrid was very low, especially in summer. This is consistent with the
466 premise that a relevant fraction of sulphate is not locally generated, but is the result of a
467 regional background with a long range transport component.

468 These data analyses complement the process-based work carried out in London in the
469 REPARTEE experiments (Harrison et al., 2012b). Campaign-based measurements using both
470 ground-based and an elevated sampling platform showed the influence of regional transport of
471 sulphate upon sulphate concentrations in London, with concentrations aloft exceeding those at
472 ground-level during an episode. On the other hand, nitrate fluxes were less clearly uni-
473 directional and were much influenced by the potential of ammonium nitrate for
474 dissociation/association (Harrison et al., 2012b). The diurnal processes involved in transfer of
475 nitrate between the condensed and vapour phases were clearly observed using single particle
476 mass spectrometry (Dall'Osto et al. 2009) and the potential for nitrate formation via NO₃ and
477 N₂O₅ was demonstrated by observations aloft on the BT Tower (ca 160 metres) (Benton et al.,
478 2010). The data analyses in this paper show strong seasonal influences, upon nitrate
479 especially, and that behaviour seen in London is not representative of that in Madrid. The
480 overall conclusion is therefore that the processes controlling nitrate and sulphate
481 concentrations may vary substantially across Europe and hence observations in one city
482 should not be assumed to be applicable elsewhere.

483

484 **Acknowledgments**

485This work has been supported by Spanish Ministry MICINN through the projects PROFASE
486(CGL2007-64117-CLI) and MICROSOL (CGL2011-27020). The authors acknowledge José
487Luis Mosquera and Marta G. Vivanco for their support with the topographic maps.
488Topographic data of the UK are copyright of NASA, NGA, USGS EROS, ESRI. M.A.
489Revuelta acknowledges the Ministry of Science and Innovation for their economical support
490through the FPI predoctoral grant BES-2008-007079.

491

492References

493Abdalmogith, S. S., Harrison, R. M. (2005). "The use of trajectory cluster analysis to examine
494the long-range transport of secondary inorganic aerosol in the UK." *Atmospheric Environment*
49539(35): 6686-6695.

496Artinano, B., Salvador, P., Alonso, D. G., Querol, X., Alastuey, A. (2003) "Anthropogenic
497and Natural Influence on the PM₁₀ and PM_{2.5} Aerosol in Madrid (Spain). Analysis of High
498Concentration Episodes." *Environmental Pollution* 125, no. 3: 453-65.

499Baker, J (2010). "A Cluster Analysis of Long Range Air Transport Pathways and Associated
500Pollutant Concentrations within the UK." *Atmospheric Environment* 44, no. 4: 563-71.

501Bari, A., Ferraro, V., Wilson, L. R., Luttinger, D., Husain, L. (2003). "Measurements of
502gaseous HONO, HNO₃, SO₂, HCl, NH₃, particulate sulfate and PM_{2.5} in New York, NY."
503*Atmospheric Environment* 37(20): 2825-2835.

504Barlow, J. F., Dunbar, T. M., Nemitz, E. G., Wood, C. R., Gallagher, M. W., Davies, F.,
505O'Connor, E., Harrison, R. M. (2011). "Boundary layer dynamics over London, UK, as
506observed using Doppler lidar during REPARTEE-II." *Atmospheric Chemistry and Physics*
50711(5): 2111-2125.

508Bampardimos, I., Nufer, M., Oderbolz, D. C., Keller, J., Aksoyoglu, S., Hueglin, C.,
509Baltensperger, U., Prévôt, A. S. H. (2011). "The weekly cycle of ambient concentrations and
510traffic emissions of coarse (PM₁₀–PM_{2.5}) atmospheric particles." *Atmospheric Environment*
51145(27): 4580-4590.

512Benton, A. K., Langridge, J. M., Ball, S. M., Bloss, W. J., Dall'Osto, M., Nemitz, E.,
513Harrison, R. M., Jones R. L. (2010). "Night-time Chemistry above London: Measurements of
514NO₃ and N₂O₅ from the BT Tower during REPARTEE-II." *Atmospheric Chemistry &*
515*Physics* 10: 9781-9795.

516Bigi, A., Harrison, R. M. (2010). "Analysis of the air pollution climate at a central urban
517background site." *Atmospheric Environment* 44(16): 2004-2012.

518Borge, R., Lumbreras, J., Vardoulakis, S., Kassomenos, P., Rodríguez, E. (2007). "Analysis of
519long-range transport influences on urban PM10 using two-stage atmospheric trajectory
520clusters." *Atmospheric Environment* 41(21): 4434-4450.

521Carslaw, D.C., Ropkins, K. (2011). "openair — an R package for air quality data analysis".
522Environmental Modelling & Software. In press.

523Crespi, S. N., Artinano, B., Cabal, H. (1995). "Synoptic classification of the mixed-layer
524height evolution." *Journal of Applied Meteorology* 34(7): 1666-1677.

525Dall'Osto, M., Harrison, R. M., Coe, H., Williams, P. I., Allan, J. D. (2009). "Real time
526Chemical characterization of local and regional nitrate aerosols." *Atmospheric Chemistry &
527Physics* 9: 3709-3720.

528Gómez-Moreno, F. J., Núñez, L., Plaza, J., Alonso, D., Pujadas, M., Artíñano, B. (2007).
529"Annual evolution and generation mechanisms of particulate nitrate in Madrid." *Atmospheric
530Environment* 41(2): 394-406.

531Harrison, R. M., Laxen, D., Moorcroft, S., Kieran, L. (2012a). "Processes affecting
532concentrations of fine particulate matter (PM2.5) in the UK atmosphere." *Atmospheric
533Environment* 46: 115-124.

534Harrison, R.M., Dall'Osto, M., Beddows, D. C. S., Thorpe, A. J., Bloss, W. J., Allan, J. D.,
535Coe, H., Dorsey, J. R., Gallagher, M., Martin, C., Whitehead, J., Williams, P. I., Jones, R. L.,
536Langridge, J. M., Benton, A. K., Ball, S. M., Langford, B., Hewitt, C. N., Davison, B., Martin,
537D., Petersson, K. F., Henshaw, S. J., White, I. R., Shallcross, D. E., Barlow, J.F., Dunbar, T.,
538Davies, F., Nemitz, E., Phillips, G. J., Helfter, C., Di Marco, C. F., Smith, S. (2012b).
539"Atmospheric chemistry and physics in the atmosphere of a developed megacity (London):
540An overview of the REPARTEE experiment and its conclusions." *Atmospheric Physics &
541Chemistry*: in press.

542Jones, A. M., Harrison, R. M. (2011). "Temporal trends in sulphate concentrations at
543European sites and relationships to sulphur dioxide." *Atmospheric Environment* 45(4): 873-
544882.

545Jones, A. M., Yin, J., Harrison, R. M. (2008). "The weekday-weekend difference and the
546estimation of the non-vehicle contributions to the urban increment of airborne particulate
547matter." *Atmospheric Environment* 42(19): 4467-4479.

548Long, R.W., McClenny, W.A., 2006. Laboratory and field evaluation of instrumentation for
549the semi-continuous determination of particulate nitrate (and other water soluble particulate
550components). *Journal of Air and Waste Management Association* 56, 294-305.

551Millstein, D. E., Harley, R. A., Hering, S. V. (2008) "Weekly cycles in fine particulate
552nitrate." *Atmospheric Environment* 42(4): 632-641.

553Putaud, J. P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H.,
554Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitztenberger, R.,
555Hüglin, C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau,
556G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H.,
557Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten
558Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F. (2010) "A European Aerosol
559Phenomenology – 3: Physical and Chemical Characteristics of Particulate Matter from 60
560Rural, Urban, and Kerbside Sites across Europe." *Atmospheric Environment* 44, no. 10: 1308-
56120.

562Putaud, J. P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M. C., Decesari, S.,
563Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N.,
564Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K.,
565Wiedensohler, A. "A European Aerosol Phenomenology—2: Chemical Characteristics of
566Particulate Matter at Kerbside, Urban, Rural and Background Sites in Europe." *Atmospheric*
567*Environment* 38, no. 16 (2004): 2579-95.

568Querol, X., Alastuey, A., Ruiz, C. R., Artinano, B., Hansson, H. C., Harrison, R. M., Buringh,
569E., ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P., Schneider, J. (2004) "Speciation
570and Origin of PM10 and PM2.5 in Selected European Cities." *Atmospheric Environment* 38,
571no. 38: 6547-55.

572Rattigan, O. V., Hogrefe, O., Felton, H. D., Schwab, J. J., Roychowdhury, U. K., Husain, L.,
573Dutkiewicz, V. A., Demerjian, K. L. (2006) "Multi-year urban and rural semi-continuous
574PM2.5 sulfate and nitrate measurements in New York state: Evaluation and comparison with
575filter based measurements." *Atmospheric Environment* 40: 192-205.

576Revuelta, M. A., Gómez-Moreno, F. J., Núñez, L., Salvador, P., Molero, F., Artíñano, B.
577(2011) "Temporal analysis and characterization of events of fine particulate sulfate in
578Madrid." *Proceedings of the V RECTA*. ISBN: 978-84-7834-662-2

579Rigby, M., Timmis, R., and Toumi, R. (2006) "Similarities of Boundary Layer Ventilation and
580Particulate Matter Roses." *Atmospheric Environment* 40, no. 27: 5112-24.

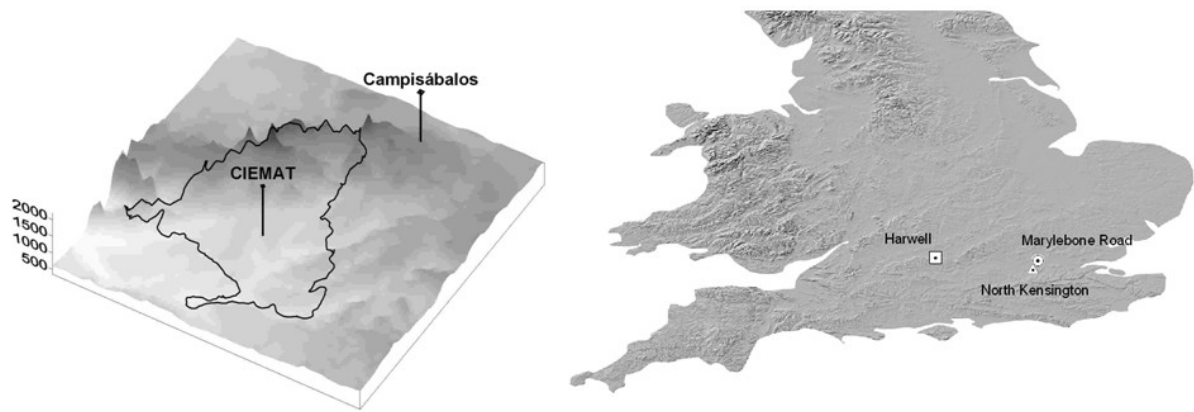
581Salvador, P., Artinano, B., Querol, X., Alastuey, A. (2008). "A combined analysis of
582backward trajectories and aerosol chemistry to characterise long-range transport episodes of
583particulate matter: the Madrid air basin, a case study." *Sci Total Environ* 390(2-3): 495-506.

584Schwab, J. J., Hogrefe, O., Demerjian, K. L., Dutkiewicz, V. A., Husain, L., Rattigan, O. V.,
585Felton, H. D. (2006). Field and laboratory evaluation of the Thermo Electron 5020 Sulphate
586Particulate Analyzer. *Aerosol Science and Technology* 40(10): 744-752.

587Wittig, A. E., Takahama, S., Khlystov, A. Y., Pandis, S. N., Hering, S., Kirby, B., Davidson,
588C. (2004) "Semi-continuous PM2.5 inorganic composition measurements during the
589Pittsburgh Air Quality Study." *Atmospheric Environment* 38(20): 3201-3213.

590**Figures**

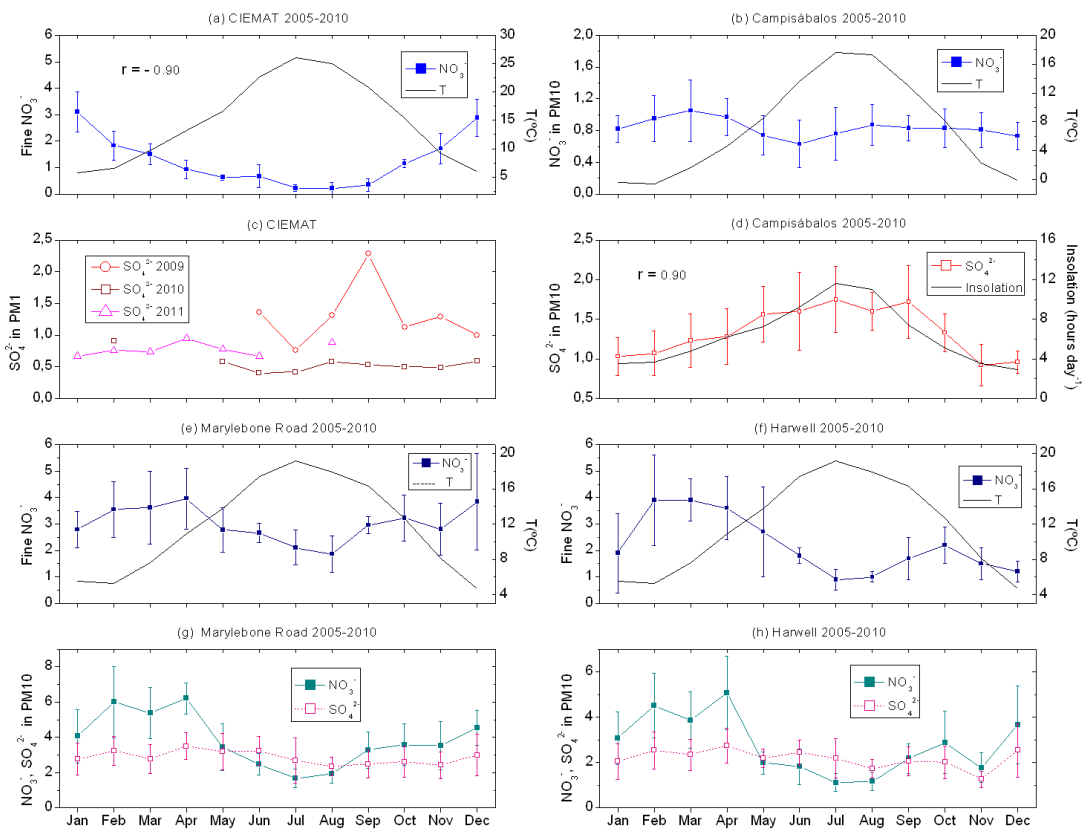
591



592**Figure 1.**

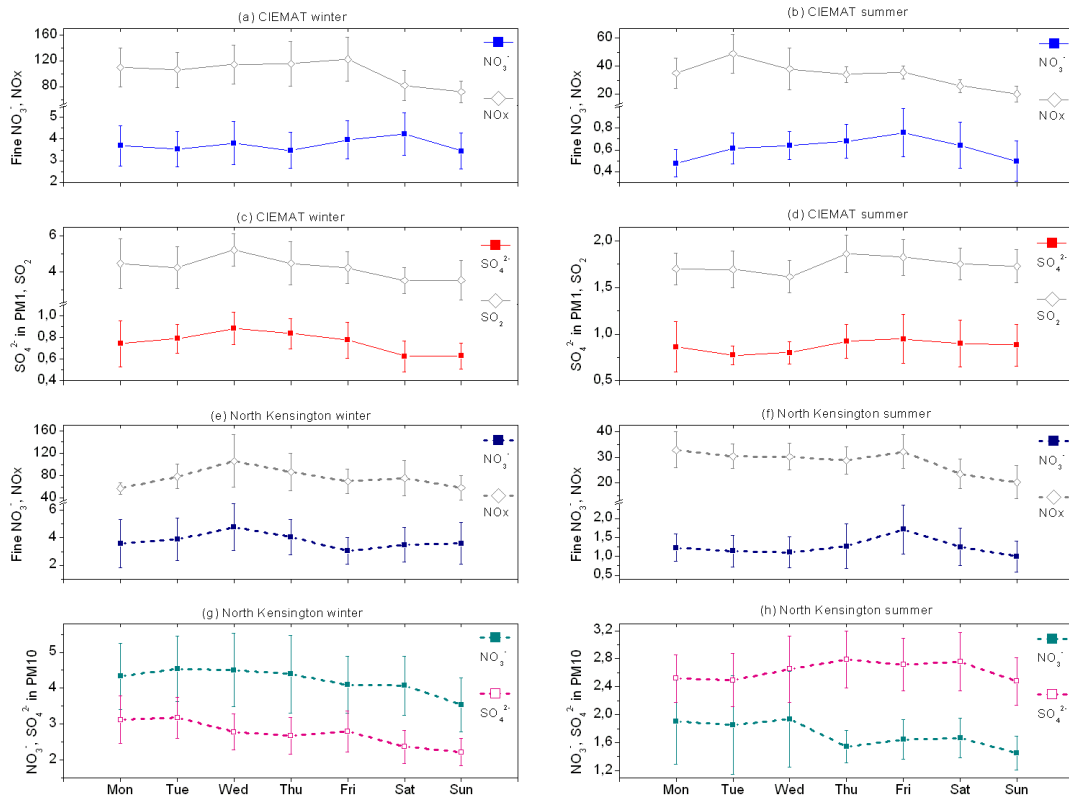
593Topographic maps of the two regions.

594



595**Figure 2.**

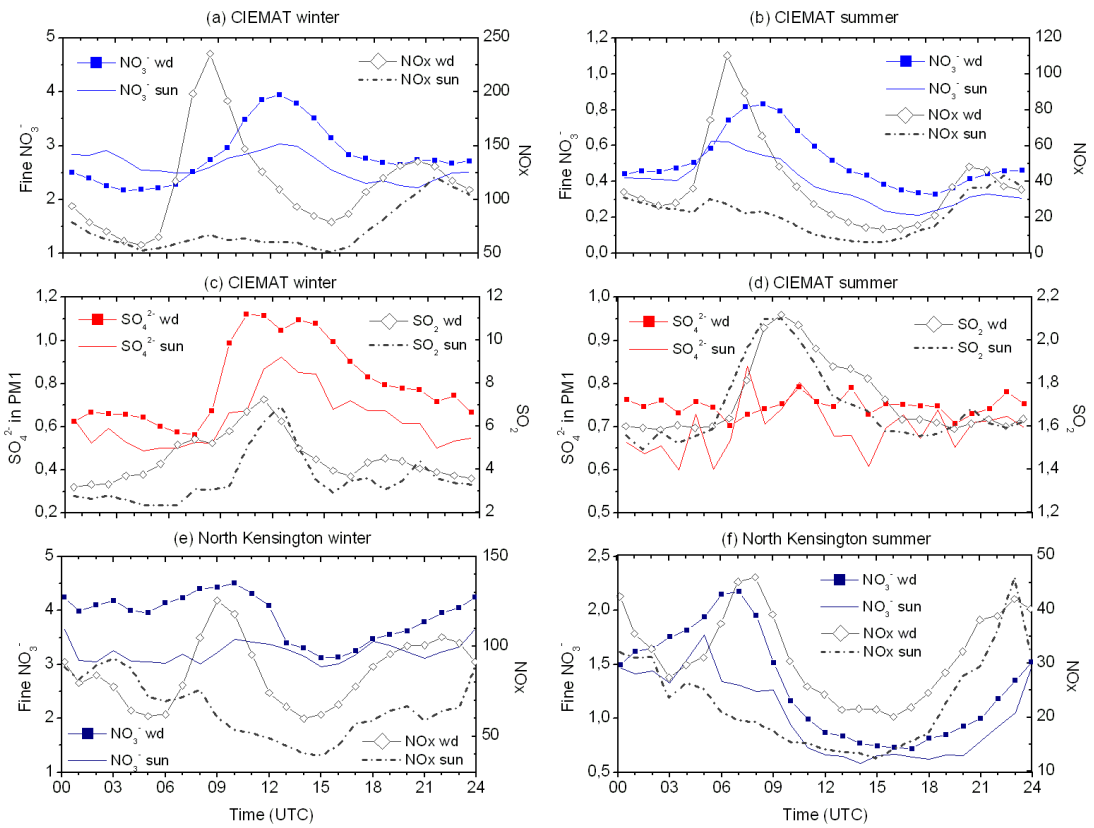
596Monthly average concentrations (in $\mu\text{g m}^{-3}$) of nitrate and sulphate in the size fractions and
597time intervals indicated.



598**Figure 3.**

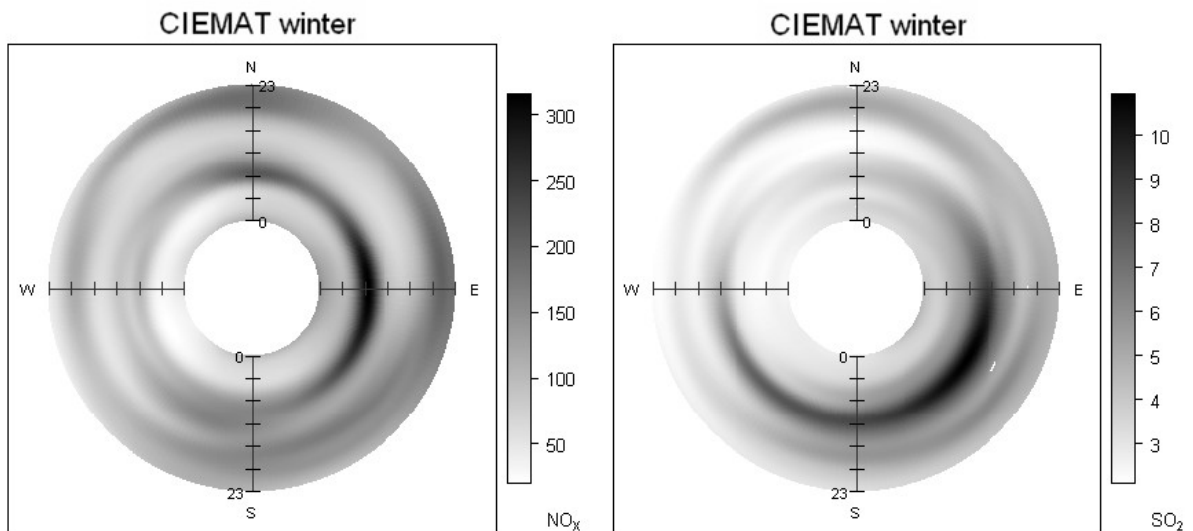
599Daily averages. (a): CIEMAT winter. Nitrate 2004/2005-2010/2011 and NO_x 2009/2010-
6002010/2011. (b): CIEMAT summer. Nitrate 2005-2011 and NO_x 2011. (c) CIEMAT winter.
601Sulphate and SO_2 2010/2011. (d) CIEMAT summer. Sulphate and SO_2 2011. (e) North
602Kensington winter. Nitrate and NO_x 2007/2008-2008/2009. (f) North Kensington summer.
603Nitrate and NO_x 2008-2009. (g) North Kensington winter. Nitrate and Sulphate 2004/2005-
6042009/2010. (h) North Kensington summer. Nitrate and Sulphate 2005-2010. Concentrations in
605 $\mu\text{g m}^{-3}$

606



607 **Figure 4.**

608 Hourly averages in concentration. Time periods correspond to Figure 3. Concentrations in μg
 609 m^{-3}
 610



611 **Figure 5.**

612Polar plots of (a) NO_x and (b) SO₂ (μg m⁻³) at the CIEMAT site in winter as a function of
613wind direction and time-of-day. Inside of circle is 00:00-01:00 h UTC running through the day
614to 23:00-24:00.

615

616**Tables**

	CIEMAT nitrate in PM2.5	CIEMAT sulphate in PM1	North K. nitrate in PM2.5	North K. sulphate in PM10
Winter				
Sat	---	18 ± 12 %	---	---
Sun	---	16 ± 15 %	---	13 ± 11 %
Mon	---	---	---	---
Summer				
Sat	---	---	---	---
Sun	18 ± 11 %	---	21 ± 16 %	---
Mon	20 ± 13 %	---	---	---

617 **Table I.**

618 Weekend reductions in SIC ± 95% CI

619

620

	NO_3^-	NO_x	$\text{NO}_3^-/\text{NO}_x$	r
Winter 2010/2011	2.60	119.24	0.03	0.74
Summer 2011	0.33	38.42	0.01	0.20

621

	SO_2	SO_4^{2-}	$\text{SO}_4^{2-}/\text{SO}_2$	r
Winter 2009/2010-2010/2011	4.32	0.88	0.29	0.31
Summer 2009	2.76	1.15	0.42	-0.13

622

	NO_3^-	SO_4^{2-}	$\text{SO}_4^{2-}/\text{NO}_3^-$	r
Winter 2009/2010-2010/2011	3.59	0.87	0.71	0.40
Summer 2009-2010	0.58	0.78	1.81	0.38

623 **Table II.**

624 Ratios $\text{NO}_3^-/\text{NO}_x$, $\text{SO}_4^{2-}/\text{SO}_2$ and $\text{SO}_4^{2-}/\text{NO}_3^-$, and correlation coefficients r in Madrid

625

626

627

628

629

630

631

632

633

634

635

636

637

638

639

640

641

642

643

644

645

646

647 **SUPPLEMENTARY INFORMATION**

648

649 **SEASONAL COMPARISON OF SIC PATTERNS IN URBAN AND RURAL SITES IN**
650 **SPAIN AND THE UK**

651

652 M.A. Revuelta, R.M. Harrison, L. Núñez, F.J. Gomez-Moreno, M. Pujadas and B. Artíñano

653

654 **North Kensington annual patterns**

655 Similar monthly averages and seasonal fine nitrate pattern in Marylebone Road and North
656 Kensington (Fig S1), although there were differences in spring. In North Kensington there are
657 only two years of data available which showed large differences on some months.

658 Similar monthly averages and seasonal PM10 nitrate and sulphate evolution in both sampling sites.

659 Figure S1

660

661 **Weekly patterns at Harwell**

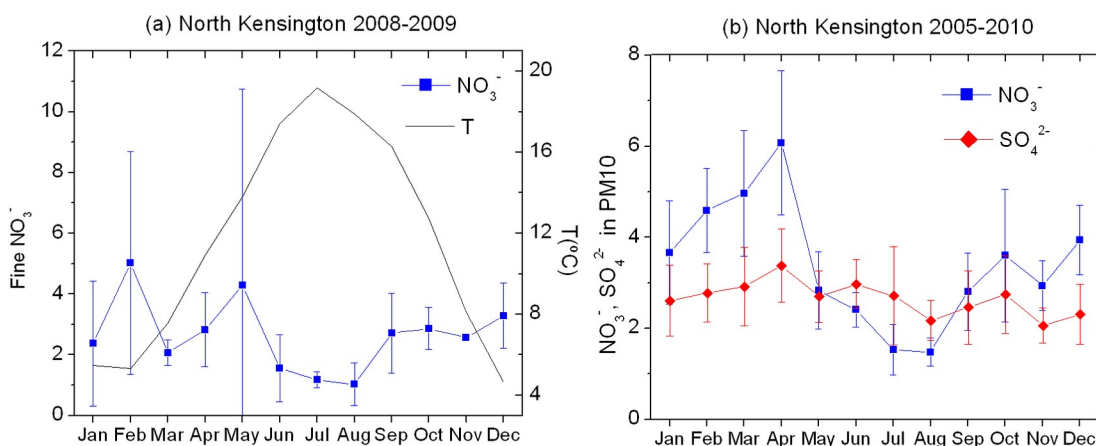
662 In the rural UK site, Harwell, NO_x levels were considerably lower than in North Kensington,
663 however, nitrate levels were not so much smaller. No statistically significant SIC weekend
664 reductions were found.

665 Figure S2

666

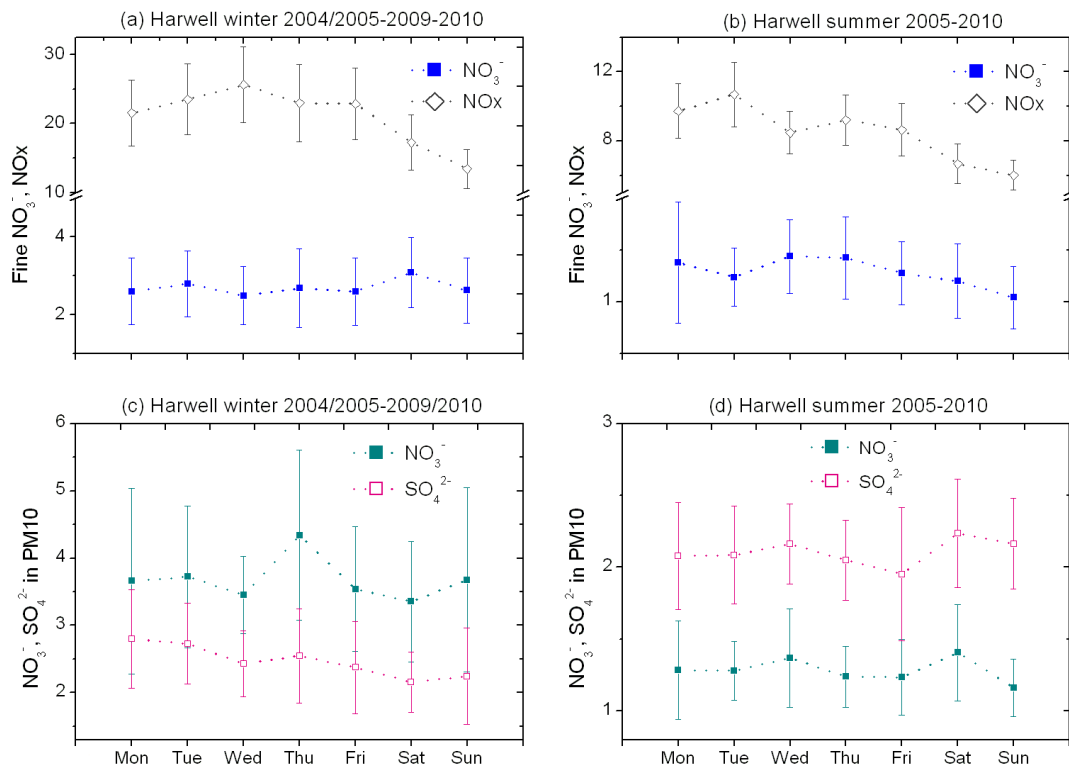
667 **FIGURES**

668



670**Figure S1:** Monthly averages in north Kensington (a) Fine nitrate and temperature. (b) Nitrate
 671and sulphate in PM10

672



673**Figure S2:** Daily averages in Harwell (a) Fine nitrate and NO_x in winter. (b) Fine nitrate and
 674 NO_x in summer. (c) Nitrate and sulphate in PM_{10} in winter. (d) Nitrate and sulphate in PM_{10}
 675in summer.

676