6                              **RESPONSE TO REVIEWERS**
7

8   **REFEREE #1**

9   *General comments:*

10  *This paper presents a study of different components of air pollution at London Heathrow*
11  *Airport in two periods covering warm and cold environmental conditions. The authors*
12  *report measurements of both particulate and gaseous pollutants and use k-means*
13  *clustering and positive matrix factorisation in an attempt to apportion measured pollution to*
14  *emissions sources and processes.*

15  *The dataset is extensive, the measurements are reliable and the analysis methods are*
16  *appropriate. However, the presentation of the study is poor and therefore, the novel*
17  *contribution of the paper is unclear. Below are major comments on the paper, after which*
18  *follow specific line-by-line comments.*

19  *The paper has a number of weaknesses, and my opinion is that major revisions are required*
20  *before it is accepted for publication.*

21  <u>Reply:</u> We would like to thank referee #1 for his/her useful comments. All the points have been
22  considered in this revised version of our manuscript. In particular, the paper was shortened and a
23  number of references were added to the "Introduction" section or moved from other sections
24  (according to the specific referee's comments). The novel contribution of this study with respect to
25  the available literature is now explained and discussed in the "Introduction" section.

26  We have organised our replies by highlighting the referee comments in bold-italic font; our reply is
27  in normal font.

28

29  *1. The literature review is incomplete and must be significantly improved. There have been*
30  *numerous studies investigating the increased concentrations of UFPs close to airports,*
31  *which must be included in the introduction. Some of these have been referenced in the*
32  *discussion of results but inclusion of these references in Introduction is required to place*
33  *this paper in the context of others and define the novel contribution.*

34  **Reply:** The "Introduction" section has been substantially amended. We have moved a whole

35  paragraph including a number of up-to-date references from "Results" to "Introduction". We have

36  also added several other references within the manuscript. We are aware that many other related

37  studies are available in the literature. However, we have cited those that might be more relevant to

38  the goals of our study. Our aim is that the current version of the "introduction" provides an

39  adequate degree of information and allows the reader to understand the state-of-the-art on the

40  topic.

41  In addition, some sentences were added to the "Introduction" to point out the novel contribution of

42  the paper with respect to the available literature. We are confident that our paper represents a

43  novel contribution to the science: the literature offers many studies on the PNC and size

44  distributions measured close or within airports. However, there are few papers using sophisticated

45  chemometric tools to quantify and characterize the airport contribution to UFPs. Air quality close to

46  large airports is potentially affected by many sources. The application of cluster and PMF analyses

47  (and the comparison of their results) allows successful extraction of the profiles of individual

48  sources. The comparison of the two methods (Section 3.3) allows the reader to understand the

49  potentials and limits of each of these source apportionment techniques.

50

51  **2. The discussion of results is not well-structured, statements are not quantified**

52  **sufficiently, and explicit references to figures are not included.**

53  *Reply:* The discussion of results has been extensively improved. Statements are now quantified.

54  Explicit references to figures and/or tables are added throughout the manuscript. We have also

55  shortened the sections related to the cluster analysis (see the referee's points 3 and 4 below).

56

57  *3. The section on the results from the k-means clustering (3.2) does not make any definitive*

58  *conclusions, and it is limited in its contribution to novel science. Most of the results are*

59  *justified by existing literature. Since that seems to be the case, the section is much longer*

60  *than is appropriate for reporting routine results. Discussion should be limited to novel*

61  *results, other results could be discussed in the SI.*

62  *Reply:* Cluster analysis extracts the most common modal spectra. It is not a novel science and it

63  has been extensively applied to PNSD, particularly in London. However, we would like to stress

64  that cluster analysis was never previously applied to 5 min resolved PNSDs in environments

65  potentially affected by airport emissions. It represents the novel application of a well consolidated

66  tool (clustering) to a specific case study (airports). In this way, we believe that its application is

67  important for this study and generates new science useful for the scientific community. In addition,

68  we believe that it is important to report the results of this technique in comparision with PMF

69  analysis (as in manuscript Section 3.3). The PNSD spectra in airport-affected environments are

70  very complex. Cluster analysis offers some simplification but was unable to resolve some of the

71  sources.

72  We agree that the discussion of the cluster analysis results is long. However, we also believe that

73  the cluster analysis gives important information and needs to be carefully discussed in the main

74  text. Following the advice of the referee, the discussion of the cluster results was improved and

75  shortened by about one third.  In particular, we have merged the discussion of the warm and cold

76  season results and have limited the main text to the main findings. We have also removed some

77  misleading sentences and some statements not well supported by the data (as pointed out by the

78  other referee).   This makes the text shorter and has streamlined the discussion.

79

80  *4. The discussion of results from the k-mean clustering and PMF analysis is repetitive and*

81  *many of the same references are used to infer the sources of particular clusters and*

82  *factors. I would suggest that the discussion of these clusters and factors is combined in*

83  *order to draw out stronger conclusions from the results (given the discussion in Section 3.3*

84  *noting good agreement between the two methods in identifying particular source*

85  *signatures). The paper would be significantly improved by removing repetition within and*

86  *the length of the Results section.*

87  *Reply:* As explained in the previous response to points 2 and 3, we have improved the sections on

88  the cluster analysis. However, these two techniques are very different (as discussed in the text)

89  and generate very different insights. Consequently, we believe that the sections cannot usefully be

90  merged. On the contrary, we prefer to consider the outcomes of each method in turn and then

91  consider what the combined data tells us about particle sources. We would like to point out that

92  referee #2 does not criticise this part. Essentially, we found that in a location with so many particle

93  source influences, clusters will never represent single source categories, whereas a well designed

94  PMF is able to better extract the profiles of individual sources.

95

96  *5. The paper is overly long and the results are not presented in a concise or coherent*

97  *manner. There are several instances of repetition.*

98  *Reply:* Several sections of the manuscript have been carefully revised according to the comments

99  of the two referees. The "Introduction" section was improved with additional references; the

100  discussion of ancillary variables (particularly for $NO_x$ and $O_3$) in the Section 3.1 "Overview of Data"

101  was removed; two figures were moved to SI, while other figures were modified following advice

from the referees; some statements in the "Results" were moved to the "Introduction"; the section on the results of the cluster analysis was shortened by ~30% by merging the results of the two seasons; statements were quantified (where possible) and references to figures and tables have been added throughout the text; we have removed several instances of repetition, errors/mistakes and misleading sentences.

Therefore, the manuscript underwent an overall shortenening and improvement, particularly in the discussion of the cluster analysis results.  We believe that the manuscript is now well balanced and the discussion streamlined.

We recognise that the manuscript is long. However, we would like to stress that most of the literature offers studies based on the application of only one source apportionment method.  This study has taken advantage of the synergy of the two methods (clustering and PMF) and their comparison. We believe that the careful discussion of outcomes from both the methods is useful and interesting for the scientific community and, therefore, needs to be preserved.

*Specific comments:*

*Line 57: The statement that aviation growth will continue for the next decade cites a study from 8 years ago. Please use a more up to date reference.*

<u>Reply:</u> Up-to-date reference added. The estimation of the current trend was recently updated by the ICAO and is approx. 5.5%/y.

*Line 69: No reference for the 'indisputable' role of LHR in driving economic affluence and vitality is given.*

<u>Reply:</u> Corrected. The whole paragraph was revised and shortened, according to the comments of the referee #2. In particular, the sentences related to the debate over the expansion of London Heathrow have been dropped off.

*Line 75: Reference(s) for arguments in support of LHR expansion?*

<u>Reply:</u> Corrected. The whole paragraph was revised and shortened, according to the comments of the referee #2. In particular, the sentences related to the debate over the expansion of London Heathrow have been dropped off.

133

***Line 82: Reference for Government approval of 3rd runway?***

**Reply:** A reference from the UK Department for Transport has been added.

136

***Line 106: Suggest present tense.***

**Reply:** Done.

139

***Line 108-117: Suggest description of methodology is moved to Section 2.***

**Reply:** This paragraph has been modified and shortened. Here, we only present the goals of the study and briefly list the adopted source apportionment methods. In addition, we have added two paragraphs pointing out the novelty of the study compared to the current literature and the secondary goal related to the analysis of the effects of a regional nucleation event.

145

***Line 119-121: Move to Acknowledgements.***

**Reply:** Done. "Classical" substituted with "Routine". These are pollutants routinely measured at DEFRA air quality sites.

149

***Line 150: Repetition.***

**Reply:** Done. The whole Materials and Methods section has been revised. In particular, the original subsection 2.1 was modified and moved to the "Introduction". All the details about the sampling campaigns are now in the new subsection 2.1 "Experimental".

154

***Line 165: Not all traffic is generated by the airport. Can the proportion be quantified?***

**Reply:** Sentence modified accordingly. Unfortunately, this is not quantifiable in this study. Our previous investigations (Masiol and Harrison, AE116, 2015) pointed out that the study of the differences (deltas) among multiple sampling sites across the study area is very useful to apportion the different sources, including traffic. However, just one site was used in this study.

160 The amended text: "The site is also affected by pollutants arising from the large volumes of road

161 traffic in London, from the local road network as well as those generated by the airport. Tunnel Rd.,

162 the main access to LHR from the M4 motorway lies 800 m west, as well as the nearby M4 (640 m

163 north) and M25 (~3.5 km east) motorways, major roads (Bath Rd, part of A4, passes 900 m south;

164 A30 lies 2.8 km SE).  The village of Harlington (~400 m west) and advection of air masses from the

165 conurbation of London are other potential external sources.".

166 ***Line 196: Suggest delete 'Classical', rephrase.***

167 **Reply:** Done.

168

169 ***Line 223: Clarify the reason for deletion of data greater than 99.5th percentile. Is this for all***

170 ***measured quantities?***

171 **Reply:** Only SMPS data have been handled in this way. Other data from the Harlington site are

172 already checked and ratified by DEFRA. We have added some sentences explaining our choice.

173 Essentially, we recognised some extreme events, which have been interpreted as outliers and/or

174 instrumental errors. Most of them were linked to unusual activities or probable instrumental issues.

175 Anyway, the modal structure of the PMF profiles with or without the removed data does not

176 change. The main reasons driving this choice were: (i) a general improvement in the stability of

177 PMF solutions; (ii) the decrease of uncertainty assessed by BS and DISP; and (iii) the decrease of

178 scaled residuals over +/-3, which, essentially, are records not well modeled by the PMF.

179 The amended text: "An in-depth analysis of the dataset revealed a few records with anomalously

180 high PNC, which were likely related to probable instrumental issues, extreme weather conditions

181 (e.g., high wind gusts, heavy rain striking the inlet), or infrequent local emissions, e.g.,

182 maintenance, painting and recreational activities (including fires) on the playground where the site

183 is located, road maintenance close the site and probable short-term parking of high-emission

184 vehicles near the site. Since this study aims to investigate the overall contributions of LHR, all data

185 are used for descriptive statistics, but data greater than the 99.5th percentile were further removed

186 for explorative, cluster and PMF analyses. This data exclusion successfully removed the extremely

187 high events occurring during the sampling campaigns and significantly improved the stability and

188 physical meaning of PMF solutions.".

189

190 ***Line 261: Figures 1 and 2 are not adequately described in the text. If the data is not worth***

191 ***mentioning in the text, the figures should be moved to the SI.***

192  **Reply:** Figure 1 (maps of area and sampling site) has been moved to SI (Figure SI1). Figure 2
193  (boxplots and diurnal patterns) was amended: now only some plots of part B (diurnal patterns) are
194  shown in the main text, while part A (boxplots) was moved to SI (Figure SI3) as well as the plots of
195  all the diurnal patterns (Figure SI4). We want to maintain some plots of the part B in the main text:
196  we believe that showing the diurnal patterns of such important variables (PNC over the three size
197  ranges, BC, solar irradiation and airport traffic) is really useful to the reader for helping the
198  interpretation of results. These patterns can be, therefore, quickly compared with those reported for
199  the clusters or the PMF factors.

200

201  *Line 288: This paragraph would be more appropriate in the Introduction.*

202  **Reply:** Done. This part was moved to the "Introduction" (also according to the main point 1 and the
203  referee #2).

204

205  *Line 312: Clarify meaning of 'intensive sampling'.*

206  **Reply:** Amended: "intensive" removed from the text.

207

208  *Line 330: Rephrase sentence 'Airport traffic undergoes: : :'*

209  **Reply:** Sentence modified accordingly: "During nighttime, airport traffic is restricted to limit noise
210  and community disturbance: …".

211

212  *Line 340: The statement that nucleation particle concentrations 'drop to near zero*
213  *overnight' is not substantiated by Figure 3. Statements discussing results must be*
214  *quantified.*

215  **Reply:** Amended. The whole paragraph was amended and the discussion of the patterns is now
216  quantified.

217

218  *Section 3.1: References to figures should be made to aid interpretation.*

219  **Reply:** Amended. The whole text was carefully revised to link sentences and discussion to the
220  appropriate figures and tables.

221

**_Line 344: From Figure 2 it is not clear that accumulation mode concentrations have a peak corresponding to the morning rush hour._**

**Reply:** The morning peak is only evident during the warm season. The sentences have been amended consequently: "Accumulation particles also present the morning (6-8 am) and evening (6-11 pm) rush hour peaks during the warm season, but only the evening peak (from 6 pm to the night) was found in the cold season (Figure 2). Generally, the evening peaks start around 6 pm, which is consistent with the peak of traffic (Figure SI5) but they extend late in the evening and night probably because the drop of the mixing layer top and the consequent concentration of pollutants close to the ground level.".

231

**_Line 421-425: Repetition, rephrase._**

**Reply:** The discussion of the cluster analysis results was strongly modified and shortened (see reply to the referee's main points 2-5). We believe that there are no repetitions in its current form.

235

**_Line 471: Clarify which clusters are being compared, 'their' is not sufficient. The comparisons between cluster 1 and cluster 5 are confused by the reference to the clusters from the warm period._**

**Reply:** Done.

240

**_Line 482: What is the basis for this interpretation? This seems to be pure speculation._**

**Reply:** We have removed the sentences and we have improved the further discussion of the two clusters in Section 3.3 (comparison of cluster analysis and PMF). This was added to the text as: "The reasons driving the split of the spectra likely to be affected by LHR into two clusters during the cold season are unclear. A further comparison of the cluster and PMF results will help in interpreting this outcome.".

247

**_Line 498: rephrase_**

**Reply:** Done. The whole section has been enhanced.

250

251 *Line 514: What is Q?*

252 **Reply:** It is the PMF objective function. In PMF, factor elements are constrained, therefore no

253 sample can have a significantly negative contribution. PMF allows each data value to be

254 individually weighted. This feature allows analysts to adjust the influence of each data point,

255 depending on the confidence in the measurement. The PMF solution minimizes the object function

256 Q via a conjugate gradient algorithm, based upon the estimated data uncertainties (or adjusted

257 data uncertainties). A quick review of the PMF and how the objective function works is reported in

258 Brown et al. (STOTEN 518-519, 2015) or in the PMF user's manual. Factor contributions and

259 profiles are therefore derived by the PMF model minimizing the objective function (Q).

260 This paragraph was moved to the "Materials and Method" section (subsection 2.2), according to

261 the following point of this referee. We have only included its name "objective function" into the text.

262 We did not provide much detail on the science behind the PMF analysis, as it is a very well

263 established technique. However, we noticed that most of the literature on PMF does not provide

264 sufficient data to describe how the model was run and what diagnostics have been taken into

265 account. In our opinion, this is a serious omission, as it is always important to know if the model is

266 performed with the optimal criteria and if the model returns acceptable diagnostics. Consequently,

267 we want to keep this (and other) brief technical information in the main text to provide all the

268 information needed by the readers/PMF analysts who want to fully reproduce/check the method.

269 This information is comparable to a QC/QA applied to the PMF analysis.

270

271 *Line 513-530: These methodological details should be in the Methods section.*

272 **Reply:** Done. Moved to "Materials and Methods" (subsection 2.2).

273

274 *Line 765: Rephrase and quantify 'well agree'.*

275 **Reply:** "well agree" was deleted. The normalised contributions are now quantified in the text and

276 some statistical tests have been also applied in the discussion of results.

277 The new paragraph is: "For the warm period, significantly higher (0.05 significance) PMF

278 contributions of the airport factor (F1) are measured for Cluster 1 (average normalised contribution

279 ~3.5). This result indicates that the airport fingerprint was well captured by both source

280 apportionment methods. During the cold season, the airport factor (F1) is significantly higher for

281 both clusters 1 and 5 (average normalised contributions of ~2 and ~3, respectively). While Cluster

282 5 presents significant high PMF contributions only for factor 1, Cluster 1 also shows high

283 contributions of factor 2 (fresh road traffic). This result indicates that Cluster 5 may be linked as the

9

typical PNSD spectra for airport emissions, while Cluster 2 likely represents mixed emissions from aircraft and airport-related traffic. A close analysis of wind roses for the two clusters in the cold season (Figure 4) reveals that Cluster 5 occurs at significantly higher wind speed regimes than Cluster 1 (Mann-Whitney-Wilcoxon test at 0.05 significance level), i.e. average wind speeds of 8.3 and 5.9 m s$^{-1}$, respectively. As a consequence, the different wind regimes may be likely responsible of the split between the two clusters.".

***Line 788-796: Literature review should be in the Introduction.***

**Reply:** Done. The whole paragraph was moved to the "Introduction".

***Line 813: Quantify 'fast drop'.***

**Reply:** Quantified. The drop was -30 µg/m$^3$ in 3 hours.

Amended sentence: "This is also supported by the PM$_{2.5}$ mass, which exhibited a rapid fall in concentrations just a few hours before the event (-30 µg m$^{-3}$ in 3 hours, i.e. from 40 µg m$^{-3}$ at 6 am to 10 µg m$^{-3}$ at 9 am, Figure 9), probably reducing the condensation sink and facilitating nucleation.".

***Line 822: Quantify 'just slightly affected'.***

**Reply:** Quantified. The whole paragraph has been re-written and now presents a large number of quantified statements and explicit references to figures.

Amended paragraph: "The results of cluster analysis were affected by the event. Before the episode, the PNSD spectra were mostly categorised as Clusters 3 and 4 (urban background and daytime pollution, respectively), i.e. the clusters mostly recorded under north-easterly wind regimes (Figure 3). About 50% and 30% of the clusters were then categorised as "airport" in the first and second hour of the episode, respectively (Figure 9). Since the wind directionality is inconsistent with an origin from the airfield, this categorisation is likely the result of the nucleation event. The growth of particles in the hours after the beginning of the event has further driven the cluster results: (i) about 60-80% of PNSDs were categorised as "fresh road traffic" (Cluster 5) after 2-3 hours, and (ii) 80-100% of PNSDs were clustered as "nighttime regional pollution" (Cluster 2) after 4-6 hours. In a similar way, PMF results were affected by the event (Figure 9), with a sharp increase of contribution levels for: (i) factor 1 (airport) from 1.5 x 10$^3$ particles cm$^{-3}$ at noon to 13.3 x 10$^3$ particles cm$^{-3}$ at 2 pm; (ii) factor 2 (fresh road traffic) from 0.5 x 10$^3$ particles cm$^{-3}$ at 1 pm to

316      21 x $10^3$ particles cm$^{-3}$ at 3 pm; and (iii) factor 3 (aged road traffic) from 2.1 x $10^3$ particles cm$^{-3}$ at 2

317      pm to approx. 15 x $10^3$ particles cm$^{-3}$ at 5-6 pm.".

318

319      **Line 827: Quantify 'slightly affected'.**

320      <u>**Reply:**</u> Done. See our reply to the previous point.

321

322      **Line 843: 'Anomalously' implies that the measurements are flawed in some way. I do not**

323      **believe that this is the case. Rephrase.**

324      <u>**Reply:**</u> Done. "Anomalously" deleted.

325

326

327      **Line 863: Clarify 'the fingerprint of London'.**

328      <u>**Reply:**</u> Done. We have amended the sentences in the item: "An urban accumulation mode was

329      found. This source presents a wide mode between 50-150 nm and accounts for around 10% of

330      PNC. The wind directionality is consistent with the advection of air masses from London. It is more

331      evident overnight due to the drop of the mixing layer top, the subsequent increase in air pollutants

332      at ground level and the generation of nighttime secondary nitrate aerosols.".

333

334      **Figure 2: Check units of particle number concentrations – values are lower than typical**

335      **ambient concentrations of 104 part/cm3 and are inconsistent with other figures.**

336      <u>**Reply:**</u> The unit is $10^3$ particles/cm$^3$. Corrected in Figure 2 and Figure SI4.

337

338      **Figure 10: This could be moved to the SI as discussion of it is very brief. Supplementary**

339      **material: This is not referenced in the main text. It is also lacking any descriptive text and is**

340      **just a collection of figures. This does not provide the reader with accessible or helpful**

341      **information.**

342      <u>**Reply:**</u> Figure 10 (now Figure 9) is important for the discussion. Most of Section 3.4 refers to the

343      plots shown in this figure. It is referenced in the text several times and allows the reader to interpret

11

344 the effects of the nucleation event upon the cluster and PMF results. On the contrary, we moved
345 Figure 11 to SI (now Figure SI11), as its discussion is very brief.

346 All the tables and figures in the SI section are referenced in the main text.

347

348 **REFEREE #2**

349 *The manuscript describes the results from a monitoring station close to LHR airport and*
350 *uses two different analytical techniques to apportion or explain the particulate matter*
351 *observed at the site. The data was collected during two intensives, nominally a warm and a*
352 *cold season. The two analysis techniques are used to estimate the influence of the airport*
353 *on the local particulate concentrations. It is clear the authors have analysed the data in*
354 *detail and the use of the two techniques to interpret the data is good, as well as*
355 *acknowledging the limitations.*

356 *Overall, I think the work is suitable for publication. I have 3 main suggestions/questions and*
357 *some detailed comments below.*

358 **Reply:** We would like to thank anonymous referee #2 for his/her very useful suggestions and the
359 general appraisal of the manuscript. Here are our answers.  We have replied point-to-point to all
360 the questions.

361 We have organised our replies by highlighting the referee comments in bold-italic font; our reply is
362 in normal font.

363 We note that a second referee has asked us to shorten the manuscript sections related to the
364 cluster analysis. We have therefore merged the discussion of the warm and cold seasons for the
365 cluster analysis and we have summarised the main findings. We are confident that the whole
366 discussion of results is now lighter, streamlined and easier to follow.

367 *Main suggestions/questions:*

368 *1) I do not think the introduction is suitable as it does not provide a good background to the*
369 *manuscript (see details below). In addition, neither the introduction or the abstract mention*
370 *the use of the regional nucleation event, which is really important for understanding a*
371 *potential limitation in the two analysis techniques*

372 **Reply:** In response to the points raised by both referees, we have extensively improved the
373 "Introduction" section. In particular, we have (i) improved the literature review by adding a number
374 of up-to-date references, (ii) improved the description of the objectives of the study, (iii) added a

discussion over the novel contribution of this study with respect to the available literature, and (iv) moved some references and text from the "results and discussion" to the "introduction".

We are confident that the current version of the "Introduction" provides all the information necessary to summarise the state-of-the-art of the research on the PNC pollution close to airports. We also believe that the improved version of the "Introduction" is able to place our study in the context of others and well defines its novel contribution to the science.

We have also added some sentences in the abstract and in the introduction presenting and describing the analysis of the strong nucleation event which occurred during the sampling campaign.

*2) I think a lot of the NOx and O3 details and graphs can be removed. The authors acknowledge that NOx has been studied in detail at the site before and the contributions from LHR to the site have been published. The paper itself is about the particulates, not air pollution in general. This would streamline the manuscript.*

**Reply:** Done. The whole subsection 3.1 was shortened and details on the $NO_x$ and $O_3$ were removed as well as Figure 2a (completely moved to SI). We have also modified the former Figure 2b (now Figure 2): now this figure shows only the variables discussed in the main text and important for the following discussion. The diurnal profiles for all the variables (former Figure 2b) has been moved to SI (new Figure SI4).

*3) What version of AIM was used to analyse the data? If it was version 10, then no action is required. If it was version 9 however, then some work is needed. There is a significant difference between V9 and V10 in the diffusional correction algorithms. V9 over estimates the size of the correction needed and can lead to an over estimation of the nanoparticles, especially below 50nm. As the authors are dividing the particles into Aikten and Ultra fine modes (and the characteristics of these modes change with season), there is a need to check as it could lead to artefacts in the clustering.*

**Reply:** We used the version 8.3, whose outputs we confirmed to be identical to the version 9. Despite the differences in the algorithm used for correcting the diffusion losses between v.10 and previous versions, TSI UK have confirmed that since we used a TSI 3080 electrostatic classifier with a long differential mobility analyser (TSI 3081), which were released with AIM v.9 we were correct to use this version of the software. In addition, since previous studies in London are also based on data extracted with those previous versions of AIM, our results are easily comparable with some of the most relevant literature.

409 **Minor question:** *Has the Aethelometer data been corrected according to Collaud Coen et al.,*
410 *2010? I note the reported protocol as defined in Petzold et al., 2015. If not, it needs*
411 *correcting especially if the authors want to draw BB aerosol information from it.*

412 **Reply:** No. Data are corrected using the WUAQL AethDataMasher V7.1 to perform data validation
413 and correct data for non-linear loading effects. We cannot apply any further correction to BC data
414 as no reference instrument was run. Anyway, we would like to point out that this study focuses on
415 the PNSDs and black carbon data are only used as ancillary variables to be related with the
416 particle sources. In addition, we would like to report that a large proportion of the black carbon data
417 in the literature are derived from aethalometers with no more than a loading correction.

418 A sentence was added to the text: "eBC was derived from the absorbance at 880 nm wavelength;
419 raw data were post-processed with the Washington University Air Quality Lab AethDataMasher
420 V7.1 to perform data validation and correct data for non-linear loading effects (Virkkula et al., 2007;
421 Turner et al., 2007).".

422

423 *Details:*

424 *I question the relevance of some of the introduction to the manuscript. Lines 75 to 83 detail*
425 *the pros and cons of a third runway, which I do not think adds to the manuscript as the*
426 *study is about the impacts of Heathrow. It is fine to say the airport is planning to increase*
427 *capacity, but as to why is not for this manuscript. In line 82, the use of the term 'Despite*
428 *this' could be misinterpreted as questioning the UK government's decision.*

429 **Reply:** A large number of sentences from this paragraph have been removed, as also
430 recommended by the comments of another referee. As a consequence "despite this" was also
431 deleted. The sentence on the future planned expansion of LHR has now a governmental reference
432 (UK Dept. for Transport).

433

434 *Lines 85 – 104 Again, I think the context of this paragraph is not appropriate for the*
435 *manuscript. The manuscript is about characterising the particulates close to Heathrow and*
436 *not about questioning EU air quality standards as there is nothing in the manuscript that*
437 *takes this data and compares mortality or morbidity predicted from these measurements*
438 *with those based on the EU standard method, for example. This section should be that*
439 *despite the UK meeting the PM standard, it has been show UFP have health issues etc and*
440 *because there is no network of measurements, campaigns such as this are key to*
441 *assessing the sources and potential impacts of airports on the UFP. The last sentence*
442 *should be removed from this section. As the authors point out (line 98), there is limited*

443 *knowledge in this area, so what should be regulated and how? EU has standards on*

444 *particulates from cars. New aircraft will soon be regulated on particulate number and mass.*

445 *EU law requires restricting exposure to nano-particles in the work place. The UK has the*

446 *clean air act. So there are policies in place, but more info in needed before guidelines and*

447 *strategies can be applied.*

448 **Reply:** The section has been comprehensively revised and shortened according to the referees'

449 comments.

450

451 *Section 2.1 – study area and dates. With the exception of the first sentence, this section*

452 *should be in the introduction. It is background and context material.*

453 **Reply:** Done.

454 *Lines 150-151, no need to repeat the dates here as they were just in the previous section.*

455 **Reply:** Done.

456

457 *Line 151-152, data from the site is QA etc. Which data? The authors or the data from the*

458 *AURN site?*

459 **Reply:** AURN site. This sentence was removed. We refer to the QA of DEFRA data later in Section

460 2.1.

461

462 *Lines 288 – 303, this reads like an introduction and is better suited in the introduction.*

463 **Reply:** Done. Moved to "Introduction", as also recommended by Referee #1.

464

465 *Section starting at line 309. This is not an acceptable way to present data and I don't see*

466 *what ranking them in order shows. This also seems to repeat a lot of information already*

467 *contained within figure 2a. Suggest removing most of that section and simply referring to*

468 *fig 2a, M&H 2015 and that the data is representative.*

469 **Reply:** Done. The "ranking" was removed. The whole section was also shortened and improved.

470 Some minor typing errors were also found and corrected.

471

472  ***Line 318, Suggest changing 'Since' to 'Analysis of the data showed it was not: : :..' and***
473  ***provide a reference for the Kruskal-Wallis analysis.***

474  **Reply:** Done: sentence modified and reference added.

475

476  ***Line 324 and figure 3. Firstly, if the PNSD are shifting towards coarser modes, how can the***
477  ***PVSD be almost constant? The author's choice of wording is contradictory. Secondly, in***
478  ***the summer it appears the mode during the day could be anywhere between 20 and 50nm***
479  ***and during the night it is around 35nm. Is the statement backed up by fitting a double log-***
480  ***normal to the data? Thirdly, why aren't the percentiles for the PVSD presented if they are***
481  ***shown for the PNSD? Finally, why are the medians presented and not the means, which is***
482  ***more common? Does the later analysis use the means or medians? If the former, figure 3***
483  ***should show means.***

484  **Reply:** The discussion of the PNSDs and PNVDs has been improved according to the referee's
485  comments. In addition, the mode ranges presented in the text have been corrected, as highlighted
486  by the referee. We have also fitted the size spectra with lognormal curves, by using 2 to 4 curves.
487  However, we do not believe that this fitting analysis should be included in the manuscript and only
488  served as a preliminarily investigation of the PNSDs.

489  This Figure (now Figure 1) was originally planned to be presented as a boxplot (where IQR (25th-
490  75th percentile range) and median are shown). This is the reason for having selected these
491  statistics. However, we recognize that it is also useful to provide the average distributions (more
492  common, but potentially affected by outliers). Therefore, we have added them for PNSD and PVSD
493  as dotted lines.

494  We only showed the IQRs for PNSD because these are the data measured by the SMPS. PNVD
495  are subsequently derived by the simple assumption that all particles are perfectly spherical (which -
496  we know- isn't true). Therefore, the modeling of PNVD is affected by a large uncertainty and in this
497  study is only used for descriptive purposes (not for quantitative analysis). Consequently, we
498  believe that it makes no sense to go into a deep analysis of the PNVD. In addition, we want to
499  keep the figures as simple as possible and the addition of other curves to the plot can mislead the
500  reader and distract from what is really important here, i.e. the PNSDs.

501  Finally, the PVSD are almost constant because the second mode of the PNSD does not change
502  during the day/night. The text has been improved accordingly.

503  The amended paragraph: "The average PNSDs are shown in Figure 2 as well as their median
504  distributions and interquartile ranges. Spectra are categorised by time of day (7am-7pm and 7pm-
505  7am local time). In addition, the particle volume size distributions (PVSDs) are also provided.

16

Results for the warm season show that the average daytime PNSD is dominated by a main peak in the nucleation range (extending below 14 nm) and a second mode in the Aitken range (between 30 and 50 nm). The nocturnal spectrum is characterised by a drop of the nucleation mode to concentration values similar to the Aitken peak (mode around 35 nm). During the cold season, the average diurnal and nocturnal PNSDs present a main peak at 15-25 nm and a second mode at 70-100 nm. In summary, both seasons show reductions of the finest modes during nighttime, while the second mode is almost constant throughout the day. As a consequence, the modal structure of PNVDs is also almost constant throughout the day.".

*Line 330, meteorology plays a role.*

**Reply:** A sentence was added to the text.

*Line 345, constant to 11pm (same value pre noon in summer)*

**Reply:** The sentence has been amended.

*Line 349, the accumulation mode peaks at around 10pm, which is inconsistent with the statement that it follows traffic which peaks at 5-6pm, for the M4 at least.*

**Reply:** An improved explanation was added. We believe that the dynamics of the mixing layer may play a role in extending the evening peaks up to the night.

The amended text: "Generally, the evening peaks start around 6 pm, which is consistent with the peak of traffic (Figure SI5) but they extend late in the evening and night probably because the drop of the mixing layer and the consequent concentration of pollutants close to ground level.".

*Line 351, I don't think the use of the word intermediate is appropriate. It is either traffic or aircraft or mixed, perhaps. Furthermore, this is interesting. Why is there a difference in winter and summer? If Version 9 of AIM was used, could this change your results if you try version 10?*

**Reply:** "Intermediate" has been replaced with "mixed". We do not attempt a further explanation of the diurnal profiles of the Aitken nuclei in this section. We limit our discussion to presentation of the results. We believe that this "mixed" behavior is related to the influence of different sources and is also complicated by the different meteorological conditions between the two seasons.

537  The amended sentences: "Aitken nuclei exhibit a mixed behaviour between nucleation and
538  accumulation particles (Figure 2): two different patterns can be found, which are more consistent
539  with road traffic in summer and with aircraft traffic in winter.".

540  We have not investigated if this pattern is also detected when using AIM10 to extract the data. We
541  believe that the manuscript should only focus on data extracted with AIM V9 (see reply to the
542  referee's main point 3).

543

544  *Lines 355 – 381. I do not think this section needs to be in the manuscript. The title of the*
545  *manuscript is about the sources of the particles near an airport. The NO2 is a) not showing*
546  *any directionality and b) has been extensively studies already. The same is true for figures*
547  *2 a and b, the NOx data can be removed from there to streamline the paper.*

548  **Reply:** We have removed the paragraphs on the $NO_x$ and $O_3$. The former Figure 2a has been
549  moved to SI. The former Figure 2b (now Figure 2) was modified to show the most important daily
550  patterns in view of the interpretation of the results. The diurnal patterns for all variables are now
551  provided in the SI.

552

553  *Line 424 – I think cluster 2 can be bi modal as well, it certainly shows in the percentiles.*

554  **Reply:** The whole section on the cluster analysis has been modified. Now, we jointly discuss
555  Cluster 2 and 3 for the warm season and the Cluster 2 for the cold season. All these clusters have
556  bimodal structures and are related to the same source.

557

558  *Line 429 – suggest changing to 'the POTENTIAL role: : :..'*

559  **Reply:** Done.

560

561  *Line 445 - again, is it mono-modal or bi-modal? The small bump at 14nm is in the median*
562  *and percentiles.*

563  **Reply:** Done. The whole section on the cluster analysis has been modified. Now, we jointly discuss
564  Cluster 5 for the warm season and the Cluster 3 for the cold season. All these clusters have a main
565  peak at 20-35 nm. We added discussion of the second possible peak of Cluster 5 within brackets.

566

567 ***Line 457 & figure 4. The hourly count for cluster 4 is very noisy. Where is the morning***
568 ***peak? The one just after 6am? I also disagree it is the mirror image of clusters 2 & 3 counts.***
569 ***It shows a broadly opposite trend. Suggest rewording.***

570 <u>Reply:</u> This was unimportant to the main purpose of the paper and has been deleted.

571 ***Cluster 1 & 5 in the cold season – It seems a little odd that the count profile of cluster 1***
572 ***matches more the profile of LHR than cluster 5, yet the suggestion is that cluster 1 is an***
573 ***aged LHR aerosol, and cluster 5 is fresh because short transit times (high wind speed).***
574 ***Surely a fresh emission will match more the LHR profile, while the process of aging will***
575 ***remove or diminish the effects of source? I don't think the author's conjecture is correct for***
576 ***cluster 5 being fresh emissions.***

577 <u>Reply:</u> We have moved our discussion on these clusters from this section to Section 3.3
578 "Comparison of k-means and PMF". This latter analysis has allowed a better interpretation of the
579 Clusters 1 and 5 (cold season). Essentially, Cluster 5 presents high contributions of the "airport"
580 source of PMF and, therefore, may represent the spectra shaped largely by the airport emissions.
581 Cluster 1 also has high contributions for the PMF factor associated with road traffic. Both are mixed
582 spectra.

583

584 ***Cluster 3 cold season – can you back up your BB conjecture with the Aeth delta C data***
585 ***averaged over the same periods? If not, you should remove it.***

586 <u>Reply:</u> There is not a significant increase of delta-C. We have therefore removed this
587 "unsupported" interpretation. We have added a revised interpretation for this result: the winter
588 mixing layer effects.

589 The amended text: "However, the diurnal pattern in winter also presents a high number of counts
590 at 3-5 am, i.e. not directly compatible with rush hours. A possible explanation involves the stronger
591 effect of the winter mixing layer dynamics on the air quality due to the presence of more frequent
592 low level thermal inversions, which may build up the pollutants at ground-level especially overnight.
593 This may increase the signal of the less intense, but still significant, nighttime traffic emissions
594 present in the study area.".

595

596 ***Line 509 replace hump with mode.***

597 <u>Reply:</u> Done.

598

**Line 581 – The contribution to the NO2 levels at LHR are quoted here as 25-30%, but in the previous section () is was found to be 15-17% from another study. Was this study different to previous ones?**

**Reply:** We have removed the sentences in line 367. We recognise that this discussion is misleading. The data refer to two different studies carried out with different apportionment methods and using data from different periods (2002-2004 and 2015-2012). In addition, we have now removed the section discussing the $NO_x$ data (see referee's main point 2).

A review of the results available in the literature is presented in the "Introduction": "For example, Carslaw et al. (2006) estimated that airport operations in 2001/4 accounted for ~27% of the annual mean $NO_x$ and $NO_2$ at the airfield boundary and less than 15% (<10 µg m$^{-3}$) at background locations 2-3 km downwind of the airport. Similar results were found for the 2008/9 period using model evaluation (AEA, 2010) and for the 2005/12 period using experimental data analysis (Masiol and Harrison, 2015). This latter study also reported that PM mass concentrations at eight sites all around LHR were always well below the EU and UK limit."

**Line 637 – 50 – 200nm is not consistent with the authors definitions of UFP (<100nm)**

**Reply:** Amended.

**Line 694 – 'to' missing from second sentence.**

**Reply:** Amended: "to" added.

**Line 711 – 3% is not modest, it is minimal.**

**Reply:** Amended, "modest" substituted with "minimal".

**Line 848 – suggest removing Anomalously . Being downwind of an airport is expected to lead to higher loadings.**

**Reply:** Done.

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629

630 # Sources of Submicrometre Particles Near a Major International Airport

631

632

633

634 **Mauro Masiol[1,2], Roy M. Harrison[1*†],**
635 **Tuan V. Vu[1], David C.S. Beddows[1]**

636

637

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## ABSTRACT
655

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656 Major airports are often located within or close to large cities; their impacts on the deterioration of

657 air quality at ground level are amply recognised. The international airport of Heathrow is a major

658 source of nitrogen oxides in the Greater London area, but its contribution to the levels of

659 submicrometre particles is unknown, and is the objective of this study. Two sampling campaigns

660 were carried out during warm and cold seasons at a site close to the airfield (1.2 km). Size spectra

661 were largely dominated by ultrafine particles: nucleation particles (<30 nm) were found to be ~10

662 times higher than those commonly measured in urban background environments of London. A set

663 of chemometric tools was used to discern the pollution arising from aircraft operations and those

664 from other sources within the city or from the traffic generated by the airport. Five clusters and 6

665 factors were identified by applying $k$-means cluster analysis and positive matrix factorization (PMF)

666 respectively to particle number size distributions; their interpretation was based on their modal

667 structures, wind directionality, diurnal patterns, road and airport traffic volumes and on the

668 relationship with weather and other air pollutants. Airport emissions, fresh and aged road traffic,

669 urban accumulation mode and two secondary sources were then identified and apportioned. The

670 comparison of cluster and PMF analyses allowed extraction of further information. ~~The analysis of~~

671 ~~a strong regional nucleation event was also performed to detect its effect upon concentrations.~~ The

672 fingerprint of Heathrow has a characteristic modal structure peaking at <20 nm and accounts for 30-

673 35% of total particles in both the seasons. Other main contributors are fresh (24-36%) and aged (16-

674 21%) road traffic emissions and urban accumulation from London (around 10%). Secondary

675 sources accounted for less than 6% in number concentrations but for more than 50% in volume

676 concentration. The analysis of a strong regional nucleation event was also performed to detect its

677 effects upon concentrations and source apportionment methods: results ~~evidenced~~showed that both

678 the cluster categorisation and PMF contributions were affected during the first 6 hours of the event.

679 In 2016, the UK government provisionally approved the construction of a third runway; therefore

680 the direct and indirect impact of Heathrow on local air quality is expected to increase unless

681 mitigation strategies are applied successfully.

22

## 1. INTRODUCTION

Emerging markets, developing economies and globalisation are drivinghave driven a fast and continuing  growth of civil aviation, which is expected to continue in the next decadelast decades (Lee et al., 2009); this trend is still growing by ~5.5% $y^{-1}$ (ICAO, 2017). As a consequence, the aircraft and road traffic at airports is also increasing, but the information available on the impact of airport emissions upon air quality at ground level is still inadequate (Webb et al., 2008; Masiol and Harrison, 2014). The quantification of airport impacts on local air quality is complicated by the complexity of multiple mobile and static emission sources, with many airports being located near to major cities, highways or industrial plants. Under this scenarioConsequently, the development of successful strategies for emission mitigation and the implementation of measures for air quality control improvement to meet regulatory standards require an exhaustivea detailed quantification of the contribution of airport and other emissions to the total air pollution load.

BiologicalLondon Heathrow (LHR) is one of the world's busiest international airports: it is ranked 1st in Europe for total passenger traffic (ACI, 2016). Its role in driving the economic affluence and vitality of the Southern UK is indisputable: it accommodates more than 1250 flights every day and serves a total of 72.3 million passengers year$^{-1}$. LHR is composed of 5 terminals and 2 runways: northern (3.9 km long) and southern (3.7 km). Currently, runways operate near their maximum capacity, with a consequent increase in the potential for delays when flights are disrupted. Since 2007, the proposal for expanding LHR with a 3rd runway and a 6th terminal has been intensely debated in UK. The main reasons supporting its expansion are: (i) the expected increase of resilience to disruption caused by congested flight traffic; (ii) the improvement of its connectivity with a profitable network of both direct long haul air routes and national flight connections; (iii) the potential to directly enhance the economic growth of the London area. On the contrary, opposition

to LHR expansion highlights the potential increases in air pollution and noise, the community destruction and argues in favour of alternative options with fewer local impacts, such as the improvement of other airports in the southern UK or the building of a new airport in the Thames Estuary (East of London). Despite this, in 2016 the UK government provisionally approved the construction of a third runway.

Greater London is one of the few UK locations not fully achieving the EU and national air quality standards: in 2015 nitrogen dioxide breached the hourly and annual limit values for health, while ozone exceeded the long-term objective (DEFRA, 2016). On the other hand, the mass concentration of particulate matter (PM), which is the standard current metric for measuring and controlling the exposure to airborne particles, was fully met for both $PM_{10}$ and $PM_{2.5}$. However, it has been widely demonstrated that even PM mass concentrations below guidelines and standards set by legislatures or international organizations may increase acute and chronic effects and mortality (e.g., Shi et al., 2015). In this situation, the use of mass concentration as a sole metric for measuring the levels or airborne particles has the disadvantage of taking greatest account of accumulation and coarse mode particles, which account for most of the mass. Consequently, the impact of the finest particles is not accounted for directly. This issue raises serious questions for the air quality standards: biological evidence associates the exposure to ultrafine particles (UFPs, <100 nm) with adverse effects upon human health (e.g., Knibbs et al., 2011; Strak et al., 2012; Ostro et al., 2015; Lanzinger et al., 2016). At the current time, there is still limited knowledge of what specific characteristic or association of characteristics may dominate the particle toxicity, and the consequent health outcomes (Atkinson et al., 2010; Strak et al., 2012, Vu et al., 2015a); nevertheless it is well recognised that UFPs can reach the deepest regions of the lung (Salma et al., 2015) and may have orders of magnitude higher surface area to mass ratios compared to larger particles. They offer more surface for the absorption of volatile and semi-volatile species (Kelly and Fussell, 2012; Strak et al., 2012). However, there are currently no ambient air quality standards or guidelines to drive the regulation of UPF.

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Several studies have reported large increases of UFPs near airports (e.g., Westerdahl et al., 2008; Hu et al., 2009; Klapmeyer et al., 2012; Hsu et al., 2012a;b). For example, Hsu et al. (2013) and Stafoggia et al. (2016) detected substantial increases of total particle number concentration (PNC) at the airports of Los Angeles (CA, USA) and Rome Ciampino (Italy), respectively, in the few minutes after take-offs, especially downwind, while landings made only a modest contribution to ground-level PNC observations. Hsu et al. (2014) observed that departures and arrivals on a major runway of Green International Airport (Warwick, RI, USA) had a significant influence on UFP concentrations in a neighborhood proximate to the end of the runway. In a study carried out at the Los Angeles international airport (CA, USA), Hudda et al. (2014) concluded that emissions from the airport increase PNC by 4- to 5-fold at 8–10 km downwind of the airfield, while Shirmohammadi et al. (2017) reported that the daily contributions of the airport to PNC were approximately 11 times greater than those from three surrounding freeways. Hudda et al. (2016) reported that average PNC were 2- and 1.33-fold higher at sites 4 and 7.3 km from the Boston (MA, USA) airport when winds were from the direction of the airfield compared to other directions. The goal of this study was to investigate the impacts of a major airport (LHR) serving a megacity (London) upon the levels of submicrometre particles and equivalent black carbon (eBC) and to apportion those impacts to aircraft, road traffic and other sources typical of large cities with airports. This task was performed by collecting air quality data at a site downwind of LHR and by applying a series of chemometric tools. The potential sources of submicron particle number concentrations (PNC) are investigated by applying two source apportionment methods: cluster analysis and positive matrix factorisation (PMF). Thus, the origin of the airport plumes was spatially assessed by matching results with local meteorological data, air mass movements, levels of common air pollutants, $PM_{2.5}$ mass concentration and its chemical speciation as an indicators of source location and formation mechanisms. Finally, the disaggregated source profiles are used to

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trace the factors affecting the pollutant levels, such as atmospheric dispersion and processing of aircraft emissions as well as of road traffic.

## 2. MATERIALS AND METHODS

### 2.1 Study Area and Dates

The summer (warm season) campaign took place from 13 August to 12 September 2014 and the winter (cold season) campaign from 19 December 2014 to 20 January 2015.

Despite the strong evidence that airports are major sources of UFPs, their fingerprint within the particle number size distribution (PNSD) may be difficult to identify due to: (i) the nature of semi-volatile compounds emitted by aircraft; (ii) the possible mechanisms of secondary aerosol formation; (iii) the dilution effect; and (iv) the similar modal structures of other emission sources concurrently found in cities, such as road traffic (Masiol and Harrison, 2014). Generally, studies performed within or close to airports have reported increases of particles ranging from 4 to 100 nm in diameter and mostly distributed in the nucleation range (<30 nm). For example, Mazaheri et al. (2009) showed a main nucleation mode and an accumulation mode (40-100 nm) more evident during take-offs; Keuken et al. (2015) reported PNSD dominated by 10-20 nm particles in an area affected by emissions from Schiphol airport (The Netherlands); Hudda and Fruin (2016) found strong increases in particles smaller than 40 nm downwind from the Los Angeles International Airport; Ren et al. (2016) showed that particles peaking at 16 nm dominate the PNSD at various distances from the runway of Tianjin International Airport, China; Masiol et al. (2016) reported that the fingerprint of aircraft emissions sampled under real ambient conditions at the airport of Venice

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(Italy) ~~have~~has a main mode at approx. 80 nm and a second mode in the nucleation range below 14 nm.

The Greater London area ~~hosts~~ is home to more than 8.5 million inhabitants and is one of the few UK locations not fully achieving the EU and national air quality standards: in 2015 nitrogen dioxide breached the hourly and annual limit values for health, while ozone exceeded the long-term objective (DEFRA, 2016). However, the standards were fully met for both $PM_{10}$ and $PM_{2.5}$.

London Heathrow (LHR) is one of the world's busiest international airports: it is ranked 1st in Europe for total passenger traffic (ACI, 2016). It accommodates more than 1250 flights every day and serves a total of 72.3 million passengers year$^{-1}$. LHR is composed of 5 terminals and 2 runways: northern (3.9 km-long) and southern (3.7 km). Currently, runways operate near their maximum capacity, with a consequent increase in the potential for delays when flights are disrupted. Since 2007, the proposal for expanding LHR with a 3rd runway and a 6th terminal has been intensely debated in the UK. In 2016 the UK government provisionally approved the construction of a third runway (UK Department for Transport, 2017).

LHR is located west of London (Figure ~~1~~SI1). Consequently, air quality in the surroundings of the airport may be affected by the advection of air masses from the city, with the associated high levels of pollutants emitted from traffic, energy demand for domestic heating and local industries. Airport activities may also contribute to air pollution advected to the city when LHR is upwind, with consequent potential impacts upon public health. In addition, as LHR attracts a large number of passengers and workers, the emissions from large volumes of road traffic generated by the airport and the nearby M4 and M25 motorways are difficult to discriminate from non-airport-related road traffic. Due to this complex scenario, the contribution of LHR is difficult to differentiate from the

810  urban background pollution, as already reported by previous modelling and experimental studies

811  (Farias and ApSimon, 2006; Masiol and Harrison, 2015).

812

813  Various studies have attempted to quantify the effect of LHR upon air quality, mainly focusing on

814  the nitrogen oxides ($NO_x=NO+NO_2$), which are well-known tracers for aircraft engine exhausts

815  (e.g., Herndon et al., 2008; Masiol and Harrison, 2014 and references therein), but also arise from

816  other combustion sources. For example, Carslaw et al. (2006) estimated that airport operations in

817  2001/4 accounted for ~27% of the annual mean $NO_x$ and $NO_2$ at the airfield boundary and less than

818  15% (<10 µg m$^{-3}$) at background locations 2-3 km downwind of the airport. Similar results were

819  found for the 2008/9 period using model evaluation (AEA, 2010) and for the 2005/12 period using

820  experimental data analysis (Masiol and Harrison, 2015). This latter study also reported that PM

821  mass concentrations at eight sites all around LHR were always well below the EU and UK limit.

822

823  This study aims to investigate the impacts of a major airport (LHR) serving a megacity (London)

824  upon the levels of submicrometre particles and to apportion those impacts to aircraft, road traffic

825  and other sources typical of large cities with airports. The main particle size distributions modes are

826  simplified by applying cluster analysis; then, the modal structures of the main potential sources are

827  disaggregated and the submicron particle number concentrations (PNC) are quantified through the

828  positive matrix factorisation (PMF). In addition, the origin of the airport plumes was spatially

829  assessed by matching results with local meteorological data, air mass movements, levels of

830  common air pollutants, $PM_{2.5}$ mass concentration and its chemical speciation as an indicators of

831  source location and formation mechanisms.

832

833  The atmospheric chemistry and physicals properties of UFPs werehave been extensively

834  investigated in London (e.g., Harrison et al., 2012; Jones et al., 2012; von Bismarck-Osten et al.,

835  2013) with several studies  using cluster analysis (Beddows et al., 2009; Brines et al., 2014; 2015)

or PMF (Beddows et al., 2015; Vu et al., 2016). However, this study is the first one carried out in South-West London to characterise and quantitatively apportion the impacts of LHR under real ambient conditions. Moreover, only one earlier study (Masiol et al., 2016) ~~jointly~~has use~~ds~~ both cluster analysis and PMF to directly assess the airport contributions to UFPs. In addition, this study also investigate~~ds~~ the effects of a regional nucleation event on the results of the two source apportionment methods.

~~Regional photochemical nucleation episodes are regularly recorded in the Southern and Eastern UK. Their general characteristics have been reported in a number of studies (e.g., Alam et al., 2003; Charron et al., 2007;2008; Beddows et al., 2015; Vu et al., 2016) and can be summarised as follows: (i) particle modality at around 20 nm; (ii) higher frequency around noon in association with the peak in actinic flux intensities; (iii) clear seasonal cycles (higher average contribution levels in the summer, from June to September); (iv) marked directionality from the westerly sectors, reflecting maritime atmospheric circulation regimes, with high wind speed and low $PM_{2.5}$ concentrations.~~

**2.      MATERIALS AND METHODS**

**2~~      Site Description~~.1   Experimental**

Two ~~intensive~~ sampling campaigns (each 1 month-long) were carried out during warm (August-September 2014) and cold (December 2014-January 2015) periods at Harlington (Figure ~~1). Data from the site are quality assured as part of the UK Automatic Urban and Rural Network under the auspices of the UK Department for Environment, Food and Rural Affairs (DEFRA; http://uk-air.defra.gov.uk/) and the site~~SI1). The site was selected as well located to sample the plumes from the airport emissions~~. The site~~: it lies 1.2 km N of the northern runway and is located inside a playground, close to a secondary road and near the village of Harlington. This is the location selected for the construction of the 3rd runway. The site is categorised as "urban industrial" by DEFRA and it is therefore more indicative of community exposure rather than direct fresh aircraft

862 emissions. Consequently, it is a good point to quantify the particles generated by the airport after a

863 relatively short ageing and dispersion in the atmosphere, and is more indicative of the fingerprint of

864 aircraft emissions affecting communities than data collected alongside the runway or in the airport

865 apron areas. In addition, previous studies have reported that the site is strongly affected by the

866 plume from the airport (Carslaw et al., 2006; Masiol and Harrison, 2015). Prevailing winds from the

867 3rd and 4th quadrants are recorded in both summer and winter (Figure SI1SI2): under such

868 circulation regimes, Harlington lies just downwind of LHR. However, theThe site is also affected

869 by pollutants arising from the large volumes of road traffic ofwithin London, from the local road

870 network as well as those generated by the airport:. Tunnel Rd., the main access to LHR from the

871 M4 motorway lies 800 m west, as well as the nearby M4 (640 m north) and M25 (~3.5 km east)

872 motorways, major roads (Bath Rd, part of A4, passes 900 m south; A30 lies 2.8 km SE).  The

873 village of Harlington (~400 m west) and advection of air masses from the conurbation of London

874 are other potential external sources.

875

876 2.3     Instrumentation Suite

877 Ultrafine particle counts and their size distributions from 14.3 to 673.2 nm were measured at 5 min

878 time resolution using a SMPS (scanning mobility particle sizer spectrometer) comprising a

879 electrostatic classifier TSI 3080 with a long differential mobility analyser (TSI 3081) and a CPC

880 (condensation particle counter, TSI 3775) based on condensation of $n$-butyl alcohol (Fisher

881 Scientific, ACS). The SMPS operated at a sheath air to aerosol flow ratio of 10:1 (sheath and

882 sample air flow rates were 3.0 and 0.3 L min$^{-1}$ respectively, voltage 10-9591 V; density 1.2 g/cc;

883 scan time 120 s, retrace 15 s;  number of scan 2) while the CPC operated at low flow rate (0.3 L

884 min$^{-1}$). The use of 5 min resolved spectra has already been used successfully for source

885 apportionment purposes at an airport (Masiol et al., 2016).

886

887    eBC was also measured at 5 min resolution using a 7-wavelength aethalometer (Magee Scientific

888    AE31). The aethalometer operated with an inlet cut-off head to collect PM with aerodynamic

889    diameter of <2.5 μm ($PM_{2.5}$). eBC was derived from the absorbance at 880 nm wavelength (Petzold

890    et al., 2013).); raw data were post-processed with the Washington University Air Quality Lab

891    AethDataMasher V7.1 to perform data validation and correct data for non-linear loading effects

892    (Virkkula et al., 2007; Turner et al., 2007).

893

894    Instruments were installed into a plastic/metal case designed for sampling purposes: (i) air inlets

895    were ~1.8 m over above the ground and were composed of conductive materials to avoid particle

896    losses and sampling artefacts; (ii) the case was cooled by fans in summer and was warmed by an

897    electrical tubular heater in winter for maintaining an indoor air temperature within an acceptable

898    range for running the equipment (temperature inside the case was recorded and periodically

899    checked); (iii) instruments were isolated from vibration using rubber pads and foam foils. Devices

900    were fully serviced, calibrated by authorised companies and underwent internal cross-calibrations

901    with other similar instruments under lab conditions. Moreover, frequent periodic checks,

902    maintenance of instruments and cleaning of inlets was performed throughout the sampling

903    campaign.

904

905    ClassicalRoutine air pollutants (NO, $NO_2$, $NO_x$, $O_3$, $PM_{10}$, $PM_{2.5}$) were measured at Harlington with

906    1 h time resolution. by the UK Automatic Urban and Rural Network under the auspices of the UK

907    Department for Environment, Food and Rural Affairs (DEFRA; http://uk-air.defra.gov.uk/).

908    Gaseous species were analysed using automatic instruments according to European standards and

909    National protocols: EN 14211:2012 for nitrogen oxides and EN 14625:2012 for ozone. $PM_{10}$ and

910    $PM_{2.5}$ were analysed using tapered element oscillating microbalance and filter dynamics

911    measurement system (TEOM-FDMS) to provide measurements accounting for volatile ($VPM_{10}$,

912    $VPM_{2.5}$) and non-volatile ($NVPM_{10}$, $NVPM_{2.5}$) fractions. Quality assurance and quality control

913  procedures followed the standards applied for the Automatic Urban and Rural Network (AURN)

914  and the London Air Quality Network (LAQN). Instruments were routinely calibrated, and every six

915  months were fully serviced and underwent intercalibration audits.

916

917  Some additional variables are also computed from the air pollutants to help the interpretation of

918  results. The $NO_2/NO_x$ ratio is indicative of the partitioning of nitrogen oxides, while the levels of

919  oxidants ($OX=O_3+NO_2$, expressed in ppbv) can be used to roughly assess the oxidative potential in

920  the atmosphere (Kley et al., 1999; Clapp and Jenkin, 2001). These two new variables are useful in

921  investigating the atmospheric chemistry behind the $NO$-$NO_2$-$O_3$ system. Delta-C (the difference

922  between absorbance at 378 and 880 nm, also called UVPM) was also computed. This variable was

923  largely used as a proxy to estimate the fraction of carbonaceous material emitted by biomass

924  burning (e.g., Sandradewi et al., 2008; Wang et al., 2011). However, Delta-C results should be used

925  with caution: Harrison et al. (2013) showed that there are probably other UV absorbing contributors

926  than wood-smoke to the aethalometer signal. This wayConsequently, Delta-C is used here only for

927  qualitative purposes.

928

929  Weather data were measured hourly by the Met Office at LHR; met data include wind direction and

930  speed, atmospheric pressure, air temperature, relative humidity (RH), visibility, rain and solar

931  irradiance.

932

933  During the two campaigns, 24-h $PM_{2.5}$ samples were also collected on quartz filters using a high

934  volume air sampler (TE-6070, Tisch Environmental, Inc.) and analysed for the daily concentrations

935  of major $PM_{2.5}$ components: organic carbon (OC) and elemental carbon (EC) by thermo-optical

936  analysis (EUSAAR_2 protocol) and major inorganic ions ($Na^+$, $K^+$, ammonium, nitrate, sulphate,

937  oxalate) by ion chromatography. Analytical methods are reported in detail in Yin et al. (2010). The

32

938 results of the chemical speciation of $PM_{2.5}$ are presented in a companion paper (in preparation) and

939 are used in this study only to assist the interpretation of PMF results.

940

941

942

943 **2.42    Data Handling and Chemometric Approaches**

944 Data were analysed using R version 3.3.1 (R Core Team, 2015) and a series of supplementary

945 packages, including 'Openair' (Carslaw and Ropkins, 2012). Preliminary data handling and clean-

946 up were carried out to check the robustness of the dataset, detect anomalous records and to delete

947 extreme outliers. SMPS data with unreliable behaviour or instrument errors were completely

948 deleted. All remainingA deepAn in-depth analysis of the dataset evidencedrevealed few records

949 with anomalously high PNC, which were likely related to probable instrumental issues, extreme

950 weather conditions (e.g., high wind gusts, heavy rain stackingstriking the inlet), or

951 uncommoninfrequent local emissions, e.g., maintenance, painting and recreational activities

952 (including fires) on the playground where the site is located, road maintenance close the site and

953 probable short-term parking of high-emission vehicles near the site. Since this study aims to

954 investigate the overall contributions of LHR, all data are used for descriptive statistics, but data

955 greater than the 99.5th percentile were further removed for explorative, cluster and PMF analyses.

956 This data exclusion successfully dropped offremoved the extremely high events occurringed during

957 the sampling campaigns and significantly improved the stability and physical meaning of PMF

958 solutions. Missing data for other variables were linearly interpolated between the nearest values of

959 the time series.

960

961 The particle number size distributions (PNSDs) were firstly grouped by applying a *k*-means cluster

962 analysis. The full method is exhaustively discussed in Beddows et al. (2009; 2014) and aims to

963 assemble single spectra into *k* clusters. The clustering groups observations with spectra similar to

33

964 their cluster centroids (means), i.e. observations that are likely generated by the same set of

965 formation processes or emission sources. The optimum number of clusters ($k$) was determined by an

966 optimisation algorithm based on the spectral shapes (Beddows et al., 2009). The choice to apply the

967 $k$-mean clustering method was based on several reasons: (i) Salimi et al. (2014) reported that $k$-

968 means is the best performing clustering among others methods tested on PNSD data; (ii) $k$-means is

969 a well-established method which has been ~~largely~~ widely applied over a number of different sites

970 (e.g., Dall'Osto et al., 2012; Wegner et al., 2012; Beddows et al., 2014; Brines et al., 2014; 2015);

971 and (iii) the method was previously applied successfully to airport data (Masiol et al., 2016).

972 PMF analysis was performed by applying the USEPA PMF5 model. Details of the PMF model are

973 reported elsewhere (Paatero and Tapper, 1994; Paatero, 1997; USEPA, 2014), while the best

974 practice and standards are extensively reviewed in several papers (e.g., Reff et al., 2007; Belis et al.,

975 2014; Brown et al., 2015; Hopke, 2016). SMPS data at 5 min resolution were used as the PMF input

976 matrix. Uncertainties associated with SMPS data were estimated according to the empirical method

977 proposed by Ogulei et al. (2007). Uncertainty for the total variable (total particle number

978 concentration, PNC) was set at 300% of the PNC concentration and also marked as "weak" to avoid

979 it driving the profiles.

980

981 The best PMF solutions were identified: (i) by investigating solutions between 3 and 10 factors; (ii)

982 by considering the minimization of the objective function $Q$ with respect to the expected

983 (theoretical) value and its stability over multiple (n=100) runs, (iii) by obtaining low values for the

984 sum of the squares of the differences in scaled residuals for each base run pair by species; (iv) by

985 minimizing the number of absolute scaled residuals over ±3 and by keeping them symmetrically

986 distributed; (v) by keeping the result uncertainties calculated by bootstrap (BS, n=200) and

987 displacement (DISP) methods within an acceptable range (Paatero et al., 2014); (vi) by obtaining

988 modelled total variable (PNC) successfully predicted ($R^2 > 0.9$ and slopes $\approx 1$); and (vii) by avoiding

the presence of edges in the G-space plots (Paatero et al., 2002) and, then, the presence of hidden/unresolved sources.

A series of additional tools were used to analyse the raw data, link source apportionment results to other variables, such as local atmospheric circulation and regional/transboundary transport of air masses. Briefly, polar plots aim to map pollutant average concentrations by wind speed and direction as continuous surfaces (Carslaw et al., 2006), while polar annuli plot by wind direction and hours of the day. The potential locations of distant sources were assessed using back-trajectory analysis and a concentration weighted trajectory (CWT) model (Stohl, 1998). Back-trajectories were computed with the HYSPLIT4 model (Stein et al., 2015; Rolph, 2016) using NCEP/NCAR reanalysis gridded meteorological data. Set-up: -96 h with a starting height of 500 m a.g.l. CWT is a method of weighting trajectories with associated concentrations to detect the most probable source areas of long-range transports of pollutants; it has been used and reviewed in a number of prior studies (e.g., Stohl, 1996; Lupu and Maenhaut, 2002; Squizzato and Masiol, 2015).

## 3. RESULTS AND DISCUSSION

### 3.1 Overview of Data

The wind roses during the two sampling periods are provided in Figure 1. Descriptive statistics of all collected variables are aggregated as boxplots in Figure 2a. Some additional variables are also computed to help the interpretation of results.SI12. Descriptive statistics of all collected variables are reported as boxplots in Figure SI3. The $NO_2/NO_x$ ratio is indicative of the partitioning of nitrogen oxides, while the levels of oxidants ($OX=O_3+NO_2$, expressed in ppbv) can be used to roughly assess the oxidative potential in the atmosphere (Kley et al., 1999; Clapp and Jenkin, 2001). These two new variables are useful in investigating the atmospheric chemistry behind the $NO-NO_2$-

35

~~O₃ system. Delta-C (the difference between absorbance at 378 and 880 nm, also called UVPM) was also computed. This variable was largely used as a proxy to estimate the fraction of carbonaceous material emitted by biomass burning (e.g., Sandradewi et al., 2008; Wang et al., 2011). However, Delta-C results should be used with caution: Harrison et al. (2013) showed that there are probably other UV absorbing contributors than wood-smoke to the aethalometer signal. This way, Delta-C is used here only for qualitative purposes.~~ PNSDs were initially split into 3 ranges: nucleation (14-30 nm), Aitken nuclei (30--100 nm) and accumulation (>100 nm). On average the total PNC during the warm season was 1.9 x $10^4$ particles $cm^{-3}$, of which 1.1 x $10^4$, 6.4 x $10^3$ and 1.5 x $10^3$ particles $cm^{-3}$ were classified as nucleation, Aitken and accumulation ranges, respectively. (Figure SI3). During the cold season, the total average PNC was 2.2 x $10^4$ particles $cm^{-3}$, composed of 1.4 x $10^4$, 6.3 x $10^3$ and 1.4 x $10^3$ particles $cm^{-3}$ as nucleation, Aitken and accumulation ranges, respectively. (Figure SI3). Concentrations lie between those of London, Marylebone Road (kerbside) and London, North Kensington (background), and nucleation particles were ~10 times higher than the annual average measured in North Kensington as reported by Vu et al. (2016), while Aitken particles were 1.9 times higher. It is therefore evident that the main difference lies in the concentration of the finest size ranges: in both seasons, spectra were dominated by UFP ($D_p$<100 nm) particles (~92% of total PNC), which only accounted for ~12% of total particle volume concentration (PVC, computed by approximation to spherical particles). On the other hand, accumulation mode particles accounted for ~8% of PNC and ~88% of PVC volume. The high levels of total PNC are not surprising: several studies carried out into or close to airports (e.g., Hsu et al., 2013;2014; Hidda et al., 2014; 2016; Stafoggia et al., 2016; Shirmohammadi et al., 2017) reported significant increases in the concentrations of UFPs.

~~The high levels of total PNC are not surprising. Several studies have reported large increases in PNC near airports. For example, Hsu et al. (2013) and Stafoggia et al. (2016) detected substantial increases of PNC values at the airports of Los Angeles (CA, USA) and Rome Ciampino (Italy),~~

~~respectively, in the few minutes after take-offs, especially downwind, while landings made only a modest contribution to ground-level PNC observations. Hsu et al. (2014) observed that departures and arrivals on a major runway of Green International Airport (Warwick, RI, USA) had a significant influence on UFP concentrations in a neighborhood proximate to the end of the runway. In a study carried out at the Los Angeles international airport (CA, USA), Hudda et al. (2014) concluded that emissions from the airport increase PNC by 4- to 5-fold at 8-10 km downwind of the airfield, while Shirmohammadi et al. (2017) reported that the daily contributions of the airport to PNC were approximately 11 times greater than those from three surrounding freeways. Hudda et al. (2016) reported that average PNC were 2- and 1.33-fold higher at sites 4 and 7.3 km from the Boston (MA, USA) airport when winds were from the direction of the airfield compared to other directions. The site used in this study is even closer to the airfield (1.2 km) and is also affected by strong non-airport sources, such as road traffic emissions due to the presence of two motorways and several busy roads (frequently congested).~~

During the ~~warm season, the average concentrations for other pollutants followed the order (in µg m$^{-3}$): NO$_x$ (49)> O$_3$ (31)> NO$_2$ (31)> PM$_{10}$ (20)> NVPM$_{10}$ (16)> PM$_{2.5}$ (14)> NO (12)> NVPM$_{2.5}$ (11)> VPM$_{10}$ (4)> VPM$_{2.5}$ (3.2)> eBC (2.4)> Delta C (<0.1). The average concentrations during the cold season were: NO$_x$ (83)> NO$_2$ (38)> O$_3$ (34)> NO (29)> PM$_{10}$ (18)> NVPM$_{10}$ (14)> PM$_{2.5}$ (13)> NVPM$_{2.5}$ (9.8)> VPM$_{10}$ (4.3)> VPM$_{2.5}$ (3.4)> eBC (2.1)> Delta C (0.2). These values are~~two sampling campaigns, air pollutants measured in Harlington (Figure SI3) were similar to the average concentrations ~~for common air pollutants~~ measured over an 8 year period (2005-2012) in the vicinity of LHR ~~reported by~~ (Masiol and Harrison ~~(,~~ 2015~~) over an 8 year period (2005-2012).~~). Consequently, despite the ~~intensive sampling campaign~~two short campaigns carried out in this study, results may be considered representative of the average levels of air pollution recorded at Harlington. The average concentrations of eBC were 2.4 and 2.1 µg m$^{-3}$ during the warm and cold

season, respectively. The average concentration of Delta-C was 0.1 µg m$^{-3}$ during the warm season and 0.36 µg m$^{-3}$ in winter.

Since

Analysis of the data were generallyshowed not a non-distributed normally,normal distribution for most of the variables: the nonparametric Kruskal-Wallis one-way analysis of variance was therefore used to test the difference of concentrations over the two periods. (Kruskal and Wallis, 1952): almost all variables are different at the 0.05 significance level, except NO, NO$_x$ and O$_3$. This result indicates a seasonal effect upon air quality in the LHR area and suggests investigating the sources over the two periods separately.

The average PNSDs are shown in Figure 31 as well as their median distributions and interquartile ranges. Spectra are categorised by time of day (7am-7pm and 7pm- 7am local time). In addition, the particle volume size distributions (PVSDs) are also provided. Results show that in both seasons the nocturnal data are shifted toward coarser modes with respect to the diurnal mean PNSD, while the modal structure of PNVDs is almost constant throughout the day. Results for the warm season show that the average daytime PNSD is dominated by a main peak in the nucleation range (extending below 14 nm) and a second mode in the Aitken range (between 30 and 50 nm). The nocturnal spectrum is characterised by a drop of the nucleation mode to concentration values similar to the Aitken peak (mode around 35 nm). During the cold season, the average diurnal and nocturnal PNSDs present a main peak at 15-25 nm and a second mode at 70-100 nm. In summary, both seasons show dropsreductions of the finest modes during nighttime, while the second mode is almost constant throughout the day. As a consequence, the modal structure of PNVDs is also almost constant throughout the day.

The diurnal cycles of most important variables the 3 particle ranges, eBC, solar irradiation and airport movements are shown in Figure 2b2. A comprehensive overview of the patterns for all the

variables is provided in Figure SI4. Generally, diurnal cycles derive from the interplay of emissions, dispersion and atmospheric chemical processes. ~~Meteorology also plays a role.~~ Consequently, they need to be investigated along with patterns for airport and motorway traffic (Figure ~~2b~~2 and Figure ~~SI2~~SI5, respectively), and as polar annuli (Figures ~~SI3~~SI6 and ~~SI4~~SI7) and polar plots (Figures ~~SI5~~SI8 and ~~SI5~~SI9), which give preliminary insights ~~upon~~ into the origin and spatial location of most probable emission sources. ~~Airport~~During nighttime, airport traffic ~~undergoes to some~~ ~~restrictions~~is restricted to limit noise and community disturbance: flights are generally constant from 6 am to 8 pm and are kept at minimum overnight, with no departures normally scheduled between 11 pm and 6 am (Figure ~~2b~~2). Road traffic is more difficult to define. Data for M4 and M25 motorways are provided by the UK Department for Transport: data for the M4 motorway show typical morning (7-8 am) and evening (5-6 pm) peaks due to rush hours, but this pattern is not well-resolved for the M25 (Figure ~~SI2~~SI5). In addition, despite it being likely that traffic on minor and local roads also follows patterns dominated by rush hours, traffic generated by the airport is more difficult to characterise, with Tunnel Rd. and other busy roads serving LHR being frequently congested.

Nucleation particles are likely associated with aircraft movements~~: the~~. The daily pattern shows high and almost constant concentrations between 7 am and ~~10~~11 pm~~, while levels~~ (Figure 2): hourly averages ranged from 10 $\times 10^3$ to 15 $\times 10^3$ particles cm$^{-3}$ during the warm season and from 10 $\times 10^3$ to 21·10$^3$ particles cm$^{-3}$ during the cold season. On the contrary, the concentrations of nucleation particles significantly (Kruskal-Wallis at $p<0.05$) drop ~~to near zero~~ overnight~~:~~ (hourly averages ranging from 5 $\times 10^3$ to 6 $\times 10^3$ particles cm$^{-3}$ and from 1 $\times 10^3$ to 5 $\times 10^3$ particles cm$^{-3}$ during the warm and cold season, respectively); the maximum average concentrations are recorded for winds blowing from the SW quadrant~~, i.e.~~ (polar plots and polar annuli in Figures SI6-9), i.e. the airfield and, in particular, the location of the main LHR terminals~~.~~ (Figure SI1). As a consequence of the dominance of nucleation particles over size spectra, also total PNC follows ~~this~~the pattern.

(Figures 2) and wind directionality (Figures SI8-9) of nucleation particles. On the contrary,

accumulation particles appear to be more associated with road traffic, i.e. daily cycles show typical

rush hour peaks and increases. These particles increase for winds blowing from northern sectors.

(Figures SI6-9), i.e. toward the M4. Accumulation particles also present the morning (6-8 am) and

evening (6-11 pm) rush hours peaks during the warm season, but only the evening peak (from 6 pm

to the night) was found in the cold season (Figure 2). Generally, the evening peaks start around 6

pm, which is consistent with the peak of traffic (Figure SI5) but they extend late in the evening and

night probably because the drop of the mixing layertop and the consequent concentration of

pollutants close to the ground level. Aitken nuclei exhibit an intermediatea mixed behaviour

between nucleation and accumulation particles. (Figure 2): two different patterns can be found,

which are more consistent with road traffic in summer and with aircraft traffic in winter.


Nitrogen oxides are key air pollutants for this study: (i) $NO_2$ levels do not fully fulfil the air quality

assessment Limit Values for health (1 h and annual mean) in the Greater London urban area

(DEFRA, 2016); (ii) they can be good tracers for airport emissions, since $NO_2$ is the main species of

nitrogen oxides emitted by turbofan engines at idle, while NO is the dominant species at higher

thrust (Wormhoudt et al., 2007; Masiol and Harrison, 2014); (iii) they are also emitted from road

traffic mainly as NO, although recent non-attainments of $NO_2$ standards in Europe have been linked

to the growing proportion of diesel-powered vehicles, which have higher primary (direct) emissions

of $NO_2$ (Carslaw et al., 2007; Grice et al., 2009; Anttila et al., 2011; Cyrys et al., 2012). In addition,

nitrogen oxides and atmospheric oxidants are strongly linked by a series of chemical reactions

which are responsible for their partitioning between NO and $NO_2$ (Finlayson-Pitts and Pitts, 2000;

Seinfeld and Pandis, 2006). To date, $NO_x$ has been thoroughly investigated at LHR (Carslaw et al.,

2006; Masiol and Harrison, 2015): it was estimated that the upper limit contribution of LHR

activities to $NO_2$ at Harlington during the 2001-2012 period was ~15-17%, while that for NO was

~10%. In this study, nitrogen dioxide exhibits two typical rush hour peaks, as previously also

40

~~observed at the London, North Kensington urban background site (Bigi and Harrison, 2010), and its~~

~~concentration increases for winds blowing from all quadrants, suggesting a mix of different sources,~~

~~including airport, road traffic and other combustion emissions. Nitric oxide only shows the morning~~

~~rush hour peak and northern directionality (toward the M4 motorway) in summer, while in winter it~~

~~lacks any significant pattern. The difference between the patterns of NO and $NO_2$ during the two~~

~~periods is also confirmed by the $NO_2/NO_x$ ratio, which shows a morning rush hour minimum in~~

~~summer as a consequence of fresh NO emissions, while it is less variable in winter (Figure 2b).~~

~~In 2015, ozone met the EU target value, but not the long-term objective in the Greater London area~~

~~(DEFRA, 2016). In this study, it does not present any wind directionality and exhibits an evident~~

~~daily peak in the mid-afternoon, i.e. when the photochemical activity is enhanced by the higher~~

~~solar irradiation and the boundary layer depth is greatest, while a second peak in the early morning~~

~~corresponds to a minimum in NO (Figure 2b).~~

Despite some studies indicating that airports are strong sources of black carbon (Dodson et al., 2009), other studies report no strong relationships with the flight activity (Masiol et al., 2016; Hsu et al.,2016). Similarly to $NO_2$ (Figure SI4) and accumulation particles (Figure 2), aethalometer data also shows typical patterns of road traffic-influenced sites for all wavelengths, with two daily peaks corresponding to the hours with higher traffic (Figure 2). However, Delta-C does not present any evident pattern (Figure SI4). eBC shows increased concentrations when winds blow from northern sectors (plus SE in winter, Figure SI7 and SI9); which excludes airport activities as being a dominant source in the study area.

Particulate matter mass concentration (PM$_{10}$ and PM$_{2.5}$) has very weak diurnal patterns (Figure SI4). Its wind directionality shows evident increases for northerly winds (Figure SI8-9). It is therefore evident that PM mass concentrations are dominated by non-airport sources, i.e. regional

1170 secondary pollutants, traffic from the nearby M4 or background pollution from London. PM$_{2.5}$

1171 concentrations normally do not exceed the Limit Values in the Greater London area (DEFRA,

1172 2016).

1173

1174 **3.2** *k*-means Cluster Analysis

1175 The clustering algorithm extracted 5 clusters for both periods. The number of clusters was selected

1176 according to the optimisation algorithm, i.e. local maxima in the Dunn indices and silhouette

1177 (Beddows et al., 2009). The extraction of 5 clusters represents a good compromise for the

1178 interpretation of spectral observations. Hussein et al. (2014) reported that is not prudent to describe

1179 the spectra with few clusters (2-4), which are not sufficient to explain variations and detailed

1180 differences in the PNSD observed in the urban atmosphere. On the other hand, they also reported

1181 that extracting too many (>10) clusters may make the aerosol source attribution more challenging.

1182

1183 The cluster centroids (mean spectra of each cluster), the 10th, 25th, 75th and 90th percentile, the

1184 hourly counts patterns and resulting wind roses are shown in ~~Figure 4~~Figures 3 and ~~5~~4 for the warm

1185 and cold season campaigns, respectively. Despite extracted clusters exhibiting significantly

1186 different modal structures for PNC, no differences can be observed for the particle volume size

1187 spectra, which all show a unimodal peak at approx. 200-300 nm. Clusters accounted for 14%-25%

1188 of total observations for both the seasons: Table SI1 summarises the percentage of the total

1189 observations for each cluster.

1190

1191 *3.2.1*Three clusters (*cluster 1, Warm season*

1192 ~~During~~during the warm season~~, 20% of total clustered observations were grouped~~ and *clusters 1*

1193 *and 5* in ~~cluster 1. It presents a~~winter) are likely shaped by the airport emissions. The modal

1194 structures present sharp ~~peak~~peaks for nucleation particles which ~~extends~~extend below the SMPS

1195 detection limit (14 nm~~),~~) and drop at 30-40 nm; no secondary modes are present in the Aitken or

accumulation ranges. These clusters show a large increase in frequency during the afternoon and evening hours (noon to 7pm) and its wind rose shows that this spectrum shape mostly occurs when the prevailing wind blows from SW.cluster 1 for the warm season and cluster 5 for the cold season) or extended over the daytime (cluster 1 for the cold season), similarly to the airport aircraft movement profiles (Figure 2). Aircraft are known to emit particles in the nucleation range (e.g. Mazaheri et al., 2009;2013; Masiol and Harrison, 2014; and references therein; Lobo et al., 2015) and the wind rose isroses are also compatible with an origin from the airfield and the main LHR terminals. (Figures 3 and 4). However, a similar PNSD profile and a similar daily pattern was also reported in North Kensington (daytime regional photochemical nucleation events in London background) by occur around noon-2 pm and are mostly recorded from June to September (Vu et al. (., 2016) and was associated with nucleation events. Its interpretation can thus). Consequently, the modal structure of cluster 1 for the warm season could be associated either with airport activities or additionally shaped by regional photochemical nucleation.

*Clusters 2 and 3* account for 19% and 23%The reasons driving the split of the spectra likely shaped by LHR into two clusters during the cold season are unclear. A further comparison of the cluster and PMF results will help in interpreting this outcome.

The modal structures of the *clusters 4* for both seasons peak for nucleation particles and extend below 14 nm, but also show probable modes between 50 and 200 nm (Figures 3 and 4). They represent the typical spectra associated with aged anthropogenic emissions, mostly due to road traffic. It is recognised that road traffic contributes to a large range (30-200 nm) of PNSD in the urban atmosphere (e.g., Yue et al., 2008; Costabile et al., 2009; Harrison et al., 2011), which is compatible with observations, respectively. While cluster 2 shows a main peak in number concentrations at 30-40 nm, cluster 3 is bimodal (14 and 60-70 nm). Both clusters exhibit similar hourly count profiles with most of the counts occurring overnight.these spectra. The directional

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analysis for the warm season shows increased levels when air masses move from the sectors more affected by traffic, i.e. London (NE), M4 (N) and M25 (W) motorways and Tunnel Rd (W), while the hour count profile presents a huge maximum during daytime. In winter, this modal structure mostly occurred for westerly winds: the atmospheric circulation during the cold season mostly experienced winds blowing from the SW quadrant, with NE sectors poorly represented (Figure SI1). As a consequence, the limited number of observations for air pollution advected from the Greater London area may have affected the detection of the urban background from London. This lack of data is also reflected by diurnal profile, which shows a marked peak in the late afternoon, concurrent to the peak of traffic on M4 and M25 (Figure SI5).

Three clusters (*clusters 2* and *3* during the warm season and *cluster 2* in winter) exhibited similar hourly profiles with most of the counts occurring overnight (Figures 3 and 4). This pattern is largely attributable to the dynamics of the mixing layer, since the diurnal cycles are the mirror image of the ambient air temperature (Figure 2b). Because of this, both clusters are strongly affected by the reduced height of the mixing layer occurring overnight. In addition, theSI4). Because of this, these clusters could be potentially affected by the reduced height of the mixing layer occurring overnight. These clusters exhibit bimodal structures with the coarser modes with respect to the remaining clusters: cluster 2 for the warm season shows a main peak in number concentrations at 30-40 nm and a second bpeak in the finest range (<16 nm), clusters 3 for the warm season peaks at 14 and 60-70 nm, and cluster 2 for the cold season extends over a wide size range with two modes around 20-30 nm and 100-150 nm.. Consequently, these clusters are likely representative of spectra mostly shaped by the drop of the mixing layer height and the formation of secondary aerosols. Under this viewIn this context, the potential role of the nighttime nitrate formation through condensation of $NH_4NO_3$ and the heterogeneous reactions of $N_2O_5$ and $NO_3$ on pre-existing particles cannot be ignored (Seinfeld and Pandis, 2006; Bertram and Thornton, 2009; Brown and Stutz, 2012). However, such The wind roses reveal that both clusters 2 occur under differentsimilar westerly

44

wind regimes. , as the wind roses indicate two different potential source locations: cluster 2 shows a with a possible origin from W sectors, while cluster 3 indicates the NE. From this we can infer that cluster 2 likely represents PNSD shaped by: (i) regional aerosols, since the wind directionality suggests an origin from regions west ofWest London, an area with a lower density of anthropogenic sources,. This way, rRegional aerosols isappear to be the most probable source. On the contrary, cluster 3 for the warm season occurs forwith winds from London (NE) and (ii) emissions from the M25 motorway and Tunnel Road, i.e. it can be influenced by aged road traffic emissions. This latter interpretation is also supported by the presence of a peak in the hourly counts corresponding to the morning rush hours. On the other hand, cluster 3 likely represents the particle size spectra mainly shaped by primary and secondary aerosols advected from the most urbanised areas, i.e. it can beis most likely associated towith the urban background of London.

The last two clusters are probably associated with road traffic: vehicle exhaust emissions peak in the Aitken and accumulation modes with the size ranging from 20 nm to 500 nm (Vu et al., 2015b, and references therein). *Cluster 5* accounts for 14% of observations and reveals a unimodal structure peaking at 25 nm. The hourly count pattern exhibits two maxima (6-8 am and 4-8 pm) related to morning and evening rush hours. The wind rose shows that observations in this clusterCluster 5 for the warm season and *cluster 3* for the cold season canmay be associated with road traffic. They reveal modal structures with a dominant peak around 20-35 nm (cluster 5 also shows a possible second peak at 15 nm) and mostly occur when air masses blow from westerly sectors, which are compatible with the location of motorways and Tunnel Rd, the main roadway linking LHR to the M4 motorway. In addition, it can be noted thatsummer, the wind rosehourly count pattern exhibits high percentages of high speed winds from W. This pattern is compatible with fresh road traffic emissions.

*Cluster 4* represents 25% of total observations. It peaks at smaller particle sizes, but also shows a wide hump at 50-150 nm. two  It is recognised that road traffic contributes to a large range (30-200 nm) of PNSD in the urban atmosphere (e.g., Yue et al., 2008; Costabile et al., 2009; Harrison et al., 2011), which is compatible with this cluster spectrum. In addition, the hour count profile presents a huge maximum during daytime with possibly 3 maxima (6-8 am and 4-8 pm) related to morning and evening rush hours plus mid-afternoon);: this pattern is the mirror image of those for clusters 2 and 3. The directional analysis shows increased levels when air masses move from the sectors more affected by traffic: London (NE), M4 (N) and M25 (W) motorways and Tunnel Rd (W). It may represent the typical spectra recorded during daytime and can be associated with aged anthropogenic emissions, mostly due to road traffic.

*3.2.2    Cold season*

Unfortunately, the atmospheric circulation during the cold season mostly experienced winds blowing from the SW quadrant, while the NE sectors were poorly represented. As a consequence, the limited extent of the wind directionality analysis may blur the interpretation of results. In addition, the limited number of observations for air pollution advected from the Greater London area may have affected the detection of the urban background.

*Clusters 1 and 5* account for 24% and 17% of total observations, respectively. They occur under comparable wind regimes (from SW) and timing (increased counts during daytime). While compatible with fresh road traffic emissions. However, the diurnal pattern of cluster 1 has the same shape as the LHR aircraft movement profiles (Figure 2), cluster 5 is more comparable with cluster 1 for the warm season (maximum in the early afternoon). However, their spectra are quite different: cluster 1 has a main mode at 20-25 nm, while cluster 5 peaks at 15 nm. Based on the prevailing wind directionality, they can both be linked to airport activities. A close analysis of wind roses reveals that cluster 5 occurs at significantly higher wind speed regimes than cluster 1 (Mann-

Whitney-Wilcoxon test at 0.05 significance level),in winter also presents a high number of counts at 3-5 am, i.e. average wind speeds of 8.3 and 5.9 m s⁻¹, respectively.not directly compatible with rush hours. A possible interpretation is that cluster 5 represents fresher airport emissions (this may also explain the high similarity with the cluster 1 for the warm season), while cluster 1 depicts the airport emissions which have undergone more aging. The aging of freshly emitted particles in the atmosphere may involve condensation, evaporation and agglomeration processes and has been demonstrated to be a major mechanism in altering aerosol PNSD (e.g., Shi et al., 1999; Kim et al., 2004; Zhang et al., 2005; Zhou et al., 2005; Zhang et al., 2011; Harrison et al., 2016); this effect was also observed for particles emitted by road traffic in London (Dall'Osto et al., 2011). Another possible interpretation is that one cluster could represent the PNSD mainly influenced by aircraft engine emissions, while the other is related to other on-airport sources, e.g., airport ground service equipment, emissions from auxiliary power units (small on-board gas turbine engines) or ground power units provided by the airport. However, this latter interpretation is less probable, since the spatial extent and temporal pattern of these two sources is the same (airfield) and, thus, they are expected to be much better mixed.

*Cluster 2* (16% of observations) extends over a wide size range (20 to 150 nm) and presents a daily pattern likely attributable to the dynamics of the mixing layer (the pattern is the mirror image of the ambient air temperature). In winter, there is a explanation involves the stronger effect of the winter mixing layer dynamics on the air quality due to the presence of more frequent low level thermal inversions, which may build up the pollutants at ground-level especially overnight. Consequently, this cluster cannot be linked to any specific primary anthropogenic sourceThis may increase the signal of the less intense, but still significant, nighttime traffic emissions present in the study area, and is likely representative of spectra mostly shaped by the drop of the mixing layer height and the formation of secondary aerosols.

*Cluster 3* accounts for 20% of data during the cold season. The size spectrum, the wind rose and, partially, the hourly count profile well relates to cluster 5 for the warm season (attributed to fresh road traffic emissions). However, the diurnal pattern also presents a high number of counts at 3-5 am, i.e. not compatible with rush hours. Wood smoke is recognised to peak around 100 nm (e.g., Chandrasekaran et al., 2013; Vu et al., 2015b). A possible interpretation is that observations included in this cluster may represent PNSDs dominated by both traffic but influenced by domestic biomass combustion.

*Cluster 4* (22%) peaks at 17 nm and also shows a wide hump at 50-150 nm. Its diurnal pattern shows a marked maximum occurring on the afternoon and is mostly represented under westerly winds regimes. Considering the differences between the two campaigns, it has similar characteristics to cluster 4 for the warm season. Thus, it can be interpreted as typical of spectra recorded during daytime and associated with the aging of anthropogenic emissions, mostly due to road traffic.

## 3.3 PMF Analysis

The best PMF solutions were identified: (i) by investigating solutions between 3 and 10 factors; (ii) by considering the minimization of the function $Q$ with respect to the expected (theoretical) value and its stability over multiple (n=100) runs, (iii) by obtaining low values for the sum of the squares of the differences in scaled residuals for each base run pair by species; (iv) by minimizing the number of absolute scaled residuals over ±3 and by keeping them symmetrically distributed; (v) by keeping the result uncertainties calculated by bootstrap (BS, n=200) and displacement (DISP) methods within an acceptable range (Paatero et al., 2014); (vi) by obtaining modelled total variable (PNC) successfully predicted ($R^2$ > 0.9 and slopes ≈1); and (vii) by avoiding the presence of edges in the G-space plots (Paatero et al., 2002) and, then, the presence of hidden/unresolved sources.

The interpretation of PMF results was then attempted by considering: (i) the knowledge of sources impacting the study area; (ii) the comparison with the results reported by Vu et al. (2016), who performed a PMF analysis of SMPS data collected in North Kensington (London urban background); (iii) the shape of resulting profiles for both the particle number and volume concentrations; (iv) the analysis of diurnal patterns; (v) the directional analysis using the polar plot and ~~CBPF~~polar annuli; (vi) the correlations between the source contributions and the other air pollutants monitored at the site or with weather variables, and (vii) the analysis of possible remote source areas by applying the CWT model.

Six-factor solutions were extracted for both the seasons. The resulting factor profiles are presented in Figures ~~6~~5 and ~~7~~6 for the warm and cold season, respectively. The factor profiles are expressed as: (i) particle number concentrations and their DISP ranges; (ii) particle volume concentrations, and (iii) explained variations showing how much of the variance (from 0 to 1) in the original dataset is accounted for by each extracted factor. The ~~figures~~Figures 5 and 6 also show the diurnal patterns and the polar plots computed ~~on~~ from the hourly-averaged contributions. Table 1 summarises the PMF results and spectral characteristics, while Table 2 shows the Pearson correlation matrices with weather and air quality variables. Selected PMF solutions were very stable: no errors or unmapped factors and few swaps (none in summer and <7% in winter) were found in BS; no swaps or errors even at $dQ_{max}$=25 were found for DISP, i.e. solutions were affected by small rotational ambiguity and, therefore, their interpretation can be considered robust.

DISP analysis is designed to explore the realistic bounds on the optimal (base run) PMF solutions that do not result in appreciable increases in the $Q$ values (Brown et al., 2015). In this study, the ranges calculated by DISP for the $dQ$=4 were used to assess the uncertainty boundaries associated ~~to~~ with the final PMF profiles, as suggested in Zikova et al. (2016) and Masiol et al. (2017). This

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1376 strategy is useful to better interpret the results, as the regions of spectra affected by high rotational

1377 ambiguity are disclosed in the resulting profiles.

1378

1379 *3.3.1    Warm season*

1380 *Factor 1* includes most of the particles in the nucleation range (<20 nm), exhibits a sharp mode in

1381 the number distribution below the SMPS detection limit (14 nm) and makes the largest contribution

1382 to the total PNC (31.6%, DISP range 31-36%) (Figure 65). However, its contribution to the volume

1383 distribution is ~1%. Several studies report that particles in the nucleation range are emitted from ~~the~~

1384 aircraft engines (e.g., Anderson et al., 2005; Herndon et al., 2008; Kinsey et al., 2010; Mazaheri et

1385 al., 2009;2013; Masiol and Harrison, 2014; Lobo et al., 2015) as well as from other anthropogenic

1386 (e.g., Schneider et al., 2005; Chen et al., 2011; Cheung et al., 2012; Stevens et al., 2012; Kumar et

1387 al., 2013;2014; Vu et al., 2015b) and natural (e.g., Kulmala et al., 1998; O'Dowd et al., 1998;1999;

1388 Kulmala and Kerminen, 2008; Riccobono et al., 2014) sources. This factor does not show any

1389 significant ($p < 0.05$) and strong ($r \geq |0.6|$) correlation with other measured species, but shows a

1390 weak ($|0.4| \leq r <|0.6|$) correlation with Factor 2. (Table 2). Its diurnal variation (Figure 65) shows

1391 higher concentrations between 6 am and 10 pm, and well agrees with the airport flight movements

1392 (Figure 2). The polar plot analysis also indicates enhanced levels when winds > 2 m s$^{-1}$ blow from

1393 the airfield sectors (SW). All these insights are consistent with the location of Heathrow, i.e. the

1394 most plausible interpretation is related to the aircraft engine exhaust emissions. This interpretation

1395 is also supported by Keuken et al. (2015), which shows that the PNSD in an area affected by

1396 emissions from Schiphol airport (The Netherlands) is dominated by ultrafine (10-20 nm) particles.

1397 The large contribution of this factor to the total PNC is not surprising if compared to the results

1398 reported for the Los Angeles international airport by Hudda et al. (2014) (emissions from the airport

1399 increased PNC 4- to 5-fold at 8–10 km downwind the airfield). Since the airport of Los Angeles and

1400 LHR have comparable aircraft traffic, the quite high concentrations found in this study (on annual

1401 average nucleation particles are ~10 times higher than those measured in North Kensington urban

1402 background by Vu et al. (2016)) are consistent with the sampling location chosen in this study (~1.2

1403 km to the airfield). In addition, this result also agrees with previous studies on the impacts of LHR

1404 on local air quality; Carslaw et al. (2006) and Masiol and Harrison (2015) found comparable

1405 percent contributions of LHR emissions on $NO_2$ levels in the study area (approx. 25-30%).

1406 However, the lack of correlations with NO and $NO_2$ (tracers for aircraft emissions) is probably due

1407 to ~~the difference in the time resolution and~~ the presence of several other sources of nitrogen oxides

1408 in the area, such as the heavy traffic generated from the airport and from the nearby motorways.

1409

1410 *Factor 2* is made up of ultrafine particles in the nucleation-Aitken range (one main peak at 20-35

1411 nm) and accounts for 28% (DISP 25-30%) of PNC; its contribution to the volume distribution is

1412 low (~2%) and peaks at 22-45 nm and at 140-220 nm~~.~~ (Figure 5; Table 1). Several insights seem to

1413 link this factor to road traffic emissions: (i) the modal structure; (ii) the strong association with

1414 morning and evening rush hours, and (iii) the significant increase for winds in the west and south-

1415 westerly sectors consistent with emissions generated from local busy roads close to LHR, Tunnel

1416 Rd. and M25 motorway. A similar mode in the nucleation range has been extensively attributed to

1417 the size distribution from road traffic (e.g., Vogt et al., 2003; Zhang et al., 2004; Ntziachristos et al.,

1418 2007; Vu et al., 2015b) and the growth of nucleation particles from diesel vehicles (Mayer and

1419 Ristovski, 2007; Wehner et al., 2009). For example, Charron and Harrison (2003) reported that

1420 particles in the range 30–60 nm show a stronger association with light-duty traffic at a traffic

1421 hotspot in central London (Marylebone Rd.); Janhäll et al. (2004) reported an average particle size

1422 distribution peaking at 15-30 nm during morning peak high traffic intensity in the city of Göteborg

1423 (Sweden), which has a car fleet comparable to the UK; Ntziachristos et al. (2007) found a sharp

1424 mode at 20-30 nm in sampling from engine exhausts. In addition, PMF factors with similar modal

1425 structures were found in other studies and were attributed to road traffic emissions: among others,

1426 Harrison et al. (2011) linked a factor peaking at 20 nm to primary road traffic emissions near a

1427 major UK highway; Masiol et al. (2016) measured PNSD in an international airport in Northern

51

1428 Italy during summer and interpreted a factor with a clear mode at 35-40 nm as road traffic from the

1429 nearby city; Beddows et al. (2015) and Vu et al. (2016) found traffic factors with modal diameter at

1430 around 30 nm in an urban background site in London (North Kensington); Sowlat et al. (2016)

1431 reported a factor peaking at 20–40 nm in number concentration and at around 30–40 nm in volume

1432 concentration in Los Angeles (US) and interpreted it as traffic tailpipe emissions. However, this

1433 factor lacks significant positive correlations with primary road traffic tracers (nitrogen oxides, eBC;

1434 Table 2), while other studies have reported weak positive correlations with such species (Harrison

1435 et al., 2011; Masiol et al., 2016; Vu et al., 2016; Sowlat et al., 2016). Similarly to factor 1, this latter

1436 result may be due to the difference in the time resolution between chemical species and PNSD and

1437 the presence of several sources of nitrogen oxides in the area.

1438

1439 *Factor 3* is mostly represented by 25–90 nm particles and contributes about 19% (17-21%) to the

1440 total number concentration. (Figure 5; Table 1). It also shows a second mode below the SMPS

1441 detection limit (14 nm), however, the DISP range clearly indicates that this part of the profile is

1442 affected by a large amount of rotational ambiguity, so that the presence of this second mode should

1443 be interpreted with caution. The volume concentration peaks at around 40–100 nm and 250–450

1444 nm. The factor contribution is higher during rush hours, but the morning peak occurs 1 h later than

1445 in factor 2. The wind directionality shows increases for air masses blowing gently ($<4$ m s$^{-1}$) from

1446 W and for calm wind periods, suggesting a quite local source; however, also an increase of

1447 concentrations is found for higher wind regimes ($>6$ m s$^{-1}$) from the East (London). Factor 3 also

1448 shows significant positive correlations with NO (0.43) and NO$_2$ (0.61) (Table 2). All these insights

1449 seem to point to an aged road traffic source. This interpretation is also supported by Vu et al.

1450 (2016), who found a similar factor in London (North Kensington) peaking at ~20–100 nm. In this

1451 context, several source apportionment studies on PNSDs have attributed more than one factor to

1452 road traffic (e.g. Kasumba et al., 2009; Thimmaiah et al., 2009; Harrison et al., 2011; Liu et al.,

1453 2014; Al-Dabbous and Kumar, 2015; Vu et al., 2016; Sowlat et al., 2016). This result is not

1454 surprising in areas where heavy traffic is widespread, as particles may undergo condensation,

1455 agglomeration, evaporation and dilution processes and, consequently, they may change modal

1456 characteristics in time and space. Such atmospheric processes are the main mechanisms reshaping

1457 PNSDs after primary exhausts are is emitted into the atmosphere and have been discussed in several

1458 studies (Shi et al., 1999; Kim et al., 2004; Zhang et al., 2005; Zhou et al., 2005; Kulmala and

1459 Kerminen, 2008; Zhang et al., 2011; Harrison et al., 2016).

1460

1461 *Factor 4* is made up of ultrafine particles over a wide range (50-200 nm with a clear mode at ~80

1462 nm for PNC and 60-300 nm for PVC). The factor contributes 14% of PNC, but accounts for the

1463 main percentage of the volume concentration (33%). This factor well correlates well with gaseous

1464 pollutants linked to combustion sources (mostly road traffic), i.e. NO (0.6), $NO_2$ (0.76), and non-

1465 volatile primary pollutants, such as eBC (0.6162), $NVPM_{2.5}$ (0.62) and EC (0.75) (Table 2). The

1466 factor also strongly correlates with OC (0.84) and sulphate (0.75). The diurnal pattern shows two

1467 main peaks in the morning and evening rush hours, (Figure 5), but the concentrations recorded

1468 between the two maxima are higher overnight than during daytime. This pattern suggests that both

1469 local emission sources and the dynamics of the mixing layer may play a key role in shaping its

1470 diurnal cycle, i.e. emitted pollutants undergo a wide dispersion within the expanded mixing layer

1471 during the daytime, while the drop of the mixing layer top occurring overnight restricts those

1472 pollutants to a layer close to ground level. The polar plot indicates increased levels for wind calm

1473 wind conditions or winds blowing from London (East sectors); in addition, the factor is strongly

1474 negatively correlated with wind speed (-0.64) (Table 2).

1475

1476 All these insights suggest that Factor 4 represents the fingerprint of the London pollution. Several

1477 studies carried out in London (Beddows et al., 2009;2015; Vu et al., 2016) and other megacities

1478 (e.g., New York: Masiol et al., 2017) have reported similar results, all interpreting this source

1479 profile as urban background (or urban accumulation mode). This source comprises both the solid

1480     particle mode from traffic emissions (Harrison et al., 2011; Pant and Harrison, 2013; Dall'Osto et

1481     al., 2012) and secondary species condensed upon pre-existing particles acting as condensation

1482     nuclei, including secondary sulphate, nitrate and organic aerosols. Secondary sulphate is formed

1483     through the atmospheric processing of local or distant $SO_2$ emissions (Kerminen et al., 2000) and

1484     neutralisation with ammonia (Benson et al., 2011). Nitrate aerosol is formed through the oxidation

1485     of $NO_2$ to nitrate and the consequent neutralization with ammonia (Seinfeld and Pandis, 2006) and

1486     occurs during both daytime and night-time; however the semivolatile nature of ammonium nitrate,

1487     makes its partitioning to the condensed-phase very weak. This behaviour also favours the

1488     occurrence of negative artefacts in filter-based sampling, which may explain the lack of significant

1489     correlations between the factor and the $PM_{2.5}$-bound nitrate (Table 2). On the contrary, the increase

1490     of the intensity of factor 4 during the night-time and the significant association with $NO_2$ are highly

1491     consistent with the chemistry driving the heterogeneous reactions of $N_2O_5$ and $NO_3$ on aerosol

1492     surfaces (Bertram and Thornton, 2009; Brown and Stutz, 2012). In view of this, Dall'Osto et al.

1493     (2009) reported that most nitrate particles in London are: (i) locally produced in urban locations

1494     during nighttime; (ii) mainly present in particles smaller than 300 nm and (iii) internally mixed with

1495     sulphate, ammonium, EC and OC.

1496

1497     Factors 5 and 6 make small contributions to PNC (4-7% and 1-4%, respectively), but are relevant

1498     for the volume concentration (37% and 21%, respectively). Factor 5 shows a main accumulation

1499     mode in number concentration at 110-250 nm and two more modes at ~30-70 nm and below 14 nm;

1500     (Figure 5; Table 1); however, the latter two modes suffer of large rotational ambiguity and should

1501     be interpreted with care. On the contrary, it exhibits a wide mode in volume concentration ranging

1502     from ~100 to ~500 nm. Factor 6 has two relevant modes in number concentration at 55-120 nm and

1503     230-400 nm, and two modes in volume concentration at 260-500 nm and 75-140 nm.

1504

1505 These factors still present two peaks corresponding to the rush hours, but the morning peak occurs

1506 1-2 h earlier than in the road traffic-related factors, i.e. when ambient temperature reaches its daily

1507 minimum. Both factors correlate well with secondary aerosol tracers (nitrate, sulphate, OC) and

1508 non-volatile components (eBC, EC, NVPM$_{2.5}$), but Factor 6 exhibits much higher correlation

1509 coefficients. (Table 2). Despite the polar plots indicating the main wind directionality toward N-E

1510 sectors, the analysis of air mass histories though the CWT model (Figure 87) clearly indicates likely

1511 continental origin areas rather than local sources.

1512

1513 Vu et al. (2016) observed two factors in North Kensington with very similar modal structures, daily

1514 patterns, correlations with PM$_{2.5}$-bound species and external source areas maps. Therefore, their

1515 interpretation is confirmed also in this study, i.e. mixed secondary aerosol (Factor 5) and inorganic

1516 secondary aerosol (Factor 6). Both factors are clearly originated from the continental Europe and

1517 are consistent with a previous receptor modelling study carried out in a rural background site

1518 representative of the southern UK (Charron et al., 2013). Similar origin and formation mechanisms

1519 also explain their strong correlation (0.75). Despite Although it is not reasonable to extract much

1520 more information from these data due to the short period into accountof sampling and the large

1521 uncertainty associated with back-trajectory analysis, it can be observed that Factor 5 shows a wide

1522 source area all over the Central Europe, while Factor 6 exhibits two distinct hotspots (Central and

1523 North-eastern Europe).

1524

1525

1526 *3.3.2 Cold season*

1527 The 6 factors identified during the cold period (Figure 76) are similar to those for the warm season.

1528 *Factor 1* is composed of a high proportion of particles in the nucleation range with a sharp mode at

1529 ~15 nm. It accounts for 33% (32-35%) of PNC and less than 2% of PVC. The polar plot reveals

1530 increased concentrations for moderate winds blowing from the airport sector and the diurnal pattern

1531 is also compatible with the aircraft traffic. No statistically significant correlations are found with

1532 any other monitored species. (Table 3). Therefore, Factor 1 may be attributed to the airport

1533 emissions related to the aircraft engine exhausts emissions. As in the warm season, factor 1 is

1534 moderately correlated with factor 2 (fresh road traffic, r=0.55), indicating a quite clear relationship

1535 between the two sources.

1536

1537 *Factor 2* represents particles in the 15-35 nm range of number concentration, accounting for 35%

1538 (33-37%) of total PNC. (Figure 6; Table 1). Its importance for volume concentration is

1539 modestminimal (3%) with two modes at 30 and 200 nm. The diurnal pattern and the wind

1540 directionality are compatible with LHR as a source and it shows a weak positive correlation with

1541 $NO_2$ (0.42) and a strong correlation with nitrate (0.63) (Table 3). Despite its similarity and

1542 relationship with Factor 1 and the consequent similar potential origin, Factor 2 may represent a

1543 different source: Factors 1 and 2 remain clearly separated even at solutions down to 4 factors,

1544 demonstrating their structural robustness and the lack of potential artefacts upon affecting the PMF

1545 solution. Consequently, it can be concluded that they to not represent over-resolved solutions (i.e.

1546 factor splitting). The most plausible interpretation for Factor 2 is therefore the same as for the warm

1547 season, i.e. fresh road traffic emissions. Furthermore, this factor can be attributed to the road traffic

1548 generated by the airport and nearby major roads.

1549

1550 *Factor 3* includes most of the particles in the Aitken range and accounts for 19% (18-20%) of PNC.

1551 It contribution to particle volume concentration is relevant (9%) with a main peak at around 100 nm

1552 and a secondary peak at 400 nm. (Table 1). It presents two rush hours peaks and the polar plot

1553 reveals an origin from the SW quadrant. However, as with the warm period, the wind directionality

1554 suggests increases for slower wind regimes than the fresh road traffic factor and for more westerly

1555 sectors, which are not compatible with the airfield location. Since factor 3 well correlates well

1556 (Table 3) with a number of other pollutants linked to primary emissions from road traffic (NO

56

1557 (0.51), NO$_2$ (0.81), eBC (0.52), PM$_{2.5}$ (0.53), OC (0.79) and EC (0.83)), it represents a second road

1558 traffic factor, more affected by aging in the atmosphere than factor 2.

1559

1560 Despite the wind regimes from NE sectors being poorly represented during the cold campaign,

1561 *Factor 4* is the only one showing a possible origin from London and for calm wind periods. As with

1562 the warm season, it is composed of a wide range of particles encompassing the Aitken and

1563 accumulation modes (50 to 150 nm), while the peak in volume concentration is at 170 nm. (Table

1564 1). The diurnal pattern (Figure 6) is clearly related to the mixing layer dynamics and the correlation

1565 analysis reveals strong relationships with many species (NO, NO$_2$, eBC, Delta-C, NVPM$_{2.5}$, OC,

1566 EC, nitrate, ammonium and potassium; Table 3). Consequently, it is concluded that it represents the

1567 urban accumulation mode, whose contribution to the total volume concentration is also similar to

1568 the warm season (33%). It is interesting to note the large similarity with the urban accumulation

1569 mode found in the warm season, from which it differs slightly only in the diurnal pattern (higher

1570 overnight) and in the presence of a strong correlation with nitrate (r=0.88), possibly due to the

1571 lesser extent of negative artefacts on PM$_{2.5}$ filter samples.

1572

1573 The last two factors are interpreted as due to secondary aerosols. Their modal structures, their

1574 contributions to total PNC and PVC, and their correlations with PM$_{2.5}$-bound species (Table 3;

1575 Figure 6) largely reflect the results obtained for the warm period. However, the CWT maps (Figure

1576 87) highlight different source areas, i.e. the origin of the secondary aerosols is regional (UK and

1577 Northern Europe). In addition, the presence of strong positive correlations with chloride may also

1578 indicate a contribution from the transport of sea-salt aerosol.

1579

1580 **3.3     Comparison of *k*-means and PMF**

1581 The cluster analysis revealed the presence of 5 characteristic PNSD shapes during both the seasons.

1582 These spectra have been linked to potential sources in the study area, i.e. road traffic, airport

activities, ~~biomass burning~~ and secondary aerosol formation processes. However, the cluster analysis is mostly driven by the ~~size~~ spectral size regions with higher particle number concentrations, i.e. it has the disadvantage of partitioning the single observations predominantly according to the finest region of the size distribution. This limitation is well illustrated by the poor (almost null) separation of clusters based on the particle volume distributions (all clusters showed quite similar particle volume spectra). In addition, cluster analysis also has the disadvantage of linking each cluster to a single source and does not easily account for PNSD resulting from the mix of two or more different sources.

In contrast, the PMF analysis computed over the PNSD also accounts well for the sources with a small impact on the number distribution, but having a larger influence on the particle volume size distributions and, therefore, on the particle mass concentration. Despite the differences in the two methods, some further information can be extracted by combining the results of cluster and PMF analysis. Figure ~~9~~8 shows the statistics of normalised PMF source contributions relating to each single cluster. ~~Generally, the two methods well agree for the "airport" source, pointing out how much the airport-related emissions may shape the PNSD in the study area.~~

For the warm period, significantly higher (0.05 significance) PMF contributions of the airport factor (F1) are measured for cluster 1~~, i.e.~~ (average normalised contribution ~3.5). This result indicates that the airport fingerprint was well ~~caught~~ captured by both source apportionment methods. During the cold season, the airport factor (F1) is significantly higher ~~during~~for both clusters 1 and 5~~.~~ (average normalised contributions of ~2 and ~3, respectively). While cluster 5 presents significant high PMF contributions only for factor 1, cluster 1 also shows high contributions of factor 2 (fresh road traffic). This result indicates that cluster 5 may be linked as the typical PNSD spectra for airport emissions, while cluster 2 likely represents mixed emissions from aircraft and airport-related traffic. A close analysis of wind roses for the two clusters in the cold season (Figure 4) reveals that

58

cluster 5 occurs at significantly higher wind speed regimes than cluster 1 (Mann-Whitney-Wilcoxon test at 0.05 significance level), i.e. average wind speeds of 8.3 and 5.9 m s$^{-1}$, respectively. As a consequence, the different wind regimes may well be likely responsible offor the split between the two clusters.

.

Results for fresh traffic emissions also agree between the two methods. Factors 2 exhibit the higher normalised contributions to clusters 5 (normalised contribution 2.5) and 1 (normalised contribution ~3) for the warm and cold period, respectively. (Figure 8). However, in winter it is evident that PNSDs grouped on cluster 1 are also strongly influenced by airport emissions, probably due to the lower mixing layer height and, thus, a lesser dispersion in the atmosphere.

Clusters 4 for both the periods show enrichments in the contributions for 4 PMF sources (aged road traffic, urban accumulation and the two secondary aerosols) (Figure 8). This further emphasises that cluster 4 represents the typical PNSD during daytime resulting from the mixing of different sources. In a similar way, clusters 3 and 2 in the warm and cold periods, respectively, represent the typical nighttime spectra, (Figures 3 and 4), i.e. they exhibit similar partitioning over the PMF sources and similar daily cycles.

## 3.4    Analysis of a Large Regional Nucleation Event

Regional photochemical nucleation episodes are regularly recorded in the Southern and Eastern UK. Their general characteristics have been reported in a number of studies (e.g., Alam et al., 2003; Charron et al., 2007;2008; Beddows et al., 2015; Vu et al., 2016) and can be summarised as follows: (i) particle modality at around 20 nm; (ii) higher frequency around noon in association with the peak in actinic flux intensities; (iii) clear seasonal cycles (higher average contribution levels in the summer, from June to September); (iv) marked directionality from the westerly sectors,

reflecting maritime atmospheric circulation regimes, with high wind speed and low PM<sub>2.5</sub>

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A strong regional nucleation event occurred during the warm period sampling campaign (starting on 7th September at 1 pm UTC and lasting for about 12 h). Increases of PNC were almost simultaneously recorded at Harlington and at Harwell, a national network rural background site located approx. 60 km WNW of LHR and representative of the regional background levels of air pollution across the Southern UK. The comparison of PNC time series at the two sites is provided as Figure SI7SI10. Figure 109 shows the contour plots of SMPS data recorded at Harlington between 7th and 8th September as well as the hourly averaged concentrations of nucleation, Aitken and accumulation particles, TEOM-FDMS $PM_{2.5}$ mass and the contributions of Factors 1 to 4 extracted by the PMF. The figureFigure 9 also reports the hourly counts of number of clusters extracted by the *k*-means analysis. The contour plot shows a typical "banana" shape with particle mode growing from ~20 nm (1 pm) to ~100 nm (overnight). The episode strongly influenced the PNSDs until around midnight; however its effect is also visible over the first half of 8th September. The time series (Figure 109) exhibits a clear peak in nucleation particles between 1 pm and 3 pm followed by peaks of Aitken (3-11 pm) and accumulation mode (8 pm-2 am) particles. The back-trajectory analysis (Figure 11SI11) has revealed that the event occurred when north-westerly fresh

60

(and clean) maritime air masses were advected from the Atlantic. This is also supported by the

$PM_{2.5}$ mass, which exhibited a fast drop of concentrations just a few hours before the event~~.~~ (-30 µg

$m^{-3}$ in 3 hours, i.e. from 40 µg $m^{-3}$ at 6 am to 10 µg $m^{-3}$ at 9 am, Figure 9), probably reducing the

condensation sink and facilitating nucleation.


Both atmospheric nucleation and aircraft engines are recognised to produce particles in the

nucleation range. The analysis of this single –but strong– episode gives insights into how much the

source apportionment results can potentially be affected by regional nucleation. This latter analysis

is possible because the wind directionality during the entire episode was from N sectors, i.e. the

contribution of LHR can be considered negligible.


The results of cluster analysis were ~~just slightly~~ affected by the event. Before the episode, the PNSD

spectra were mostly categorised as clusters 3 and 4 (urban background and daytime pollution,

respectively), ~~while a few~~i.e. the clusters ~~(less than 1 h of observations)~~mostly recorded under

north-easterly wind regimes (Figure 3). About 50% and 30% of the clusters were then categorised

as "airport" ~~during~~in the ~~beginning~~first and second hour of the episode~~.~~, respectively (Figure 9).

Since the wind directionality is inconsistent with an origin from the airfield, this categorisation is

likely the result of the nucleation event. The growing of particles in the ~~subsequent~~ hours ~~was then~~

~~identified~~after the beginning of the event has further driven the cluster results: (i) about 60-80% of

PNSDs were categorised as "fresh road traffic" (cluster 5) ~~and~~after 2-3 hours, and (ii) 80-100% of

PNSDs were clustered as "nighttime regional pollution" (cluster 2~~).~~) after 4-6 hours. In a similar

way, PMF results were ~~slightly~~ affected by the event~~.~~ (Figure 9), with a sharp increase of

contribution levels for: (i) factor 1 (airport) ~~and, then, for factors~~from 1.5-$x10^3$ particles $cm^{-3}$ at

noon to 13.3-$x10^3$ particles $cm^{-3}$ at 2 pm; (ii) factor 2 (fresh road traffic) ~~and~~ from 0.5-$x10^3$ particles

$cm^{-3}$ at 1 pm to 21-$x10^3$ particles $cm^{-3}$ at 3 pm; and (iii) factor 3 (aged road traffic~~).~~) from 2.1-$x10^3$

particles $cm^{-3}$ at 2 pm to approx. 15-$x10^3$ particles $cm^{-3}$ at 5-6 pm.

1686

1687 This episode was the main nucleation event recorded during the two sampling campaigns. Other

1688 possible episodes also occurred (mostly during the warm season), but they were much less

1689 significant and often hard to detect. This qualitative analysis points to some conclusions: (i)

1690 regional photochemical nucleation events may have an effect on clustering and PMF results; (ii) the

1691 effect may lead to an "additive" bias, mostly over the "airport" and "road traffic" factors and

1692 clusters; (iii) the effect of regional nucleation events in the study area is largely overwhelmed by the

1693 strength of local sources, but in other locations with more frequent nucleation events it may be more

1694 important to identify and separate them.

1695

1696 **4      CONCLUSIONS**

1697 The effect of airport emissions upon the particle number concentration and size distribution was

1698 assessed at a site close to a major European airport (Heathrow) serving a megacity (London).  The

1699 conclusions to be drawn are:

1700 • ~~Anomalously high~~High particle number concentrations were recorded for the finest sizes

1701   (nucleation <30 nm and Aitken nuclei 30-100 nm) if compared to an urban background site in

1702   London (N. Kensington).

1703 • Polar plot analysis indicates that Heathrow is a strong potential source for $NO_2$, nucleation and

1704   Aitken particles, but its contribution to the mass concentration of $PM_{2.5}$ and eBC is very small.

1705   On the contrary, the <u>urban area of </u>London ~~area seems ~~appears to be ~~a main ~~<u>the main </u>source for

1706   PM and eBC.

1707 • The *k*-means cluster analysis has revealed that 20% of PNSDs are mostly shaped by airport

1708   direct emissions, but particle size spectra are also strongly affected by other local sources

1709   (mostly fresh and aged road traffic during daytime) and the reduction of mixing layer depth

1710   (during nighttime). Typical PNSD spectra have been identified for nighttime and daytime

1711   pollution as well. Such spectra are likely the result of multiple source mixtures.

- PMF analysis revealed that the fingerprint of Heathrow has a peculiar modal structure peaking at <20 nm. The direct airport emissions account for 30-35% of total particles in both the seasons. Such results are in line with percent estimations for $NO_2$ reported in previous studies.

- Other major contributors to PNC are fresh (24-36%) and aged (16-21%) road traffic emissions. Despite both applied source apportionment methods failing to fully disaggregate the emissions from the local traffic (including motorway) and traffic generated by the airport, results suggest that road traffic sources may contribute to the total PNC more than Heathrow (40-56%). However, making a clear distinction between the influence of traffic generated by the airport from other road traffic is not feasible from this analysis.

- ~~The fingerprint of London has~~An urban accumulation mode was found. This source presents a wide mode between 50-150 nm.~~ This urban accumulation mode~~ and accounts for around 10% of PNC~~ and~~. The wind directionality is ~~the result of~~consistent with the advection of air masses from ~~the city~~London. It is more evident overnight due to the drop of the mixing layer top, the subsequent increase in air pollutants at ground level and the generation of nighttime secondary nitrate aerosols.

- Secondary sources accounted for less than 6% in number concentrations but for more than 50% in volume concentration. Long-range transport has a key role in advecting polluted air masses from mainland Europe.

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**TABLE LEGENDS:**

**Table 1.** Summary of PMF results for both seasons.

**Table 2.** Results of Pearson's correlation analysis among extracted factor contributions and other measured variables recorded at different time resolutions. Only correlations significant at $p<0.05$ are reported, strong correlations ($\rho>|0.6|$) are highlighted in bold.

**FIGURE LEGENDS:**

~~**Figure 1.** Map of LHR and sampling site (left) and map of the Greater London area (upper right). Wind roses calculated over the two sampling periods are also provided (bottom right). The location of some main potential sources is also highlighted: T1, T2, T3, T4 and T5 are the Heathrow terminals; TR= Tunnel Rd.~~

~~**Figure 2.** Boxplots (a) and diurnal patterns (b) of the most important measured variables (and derived variables) during the two sampling periods. All valid data are used for computing boxplot statistics: Boxplot lines= medians, crosses= arithmetic means, boxes= 25th-75th percentile ranges, whiskers= ±1.5*inter-quartile ranges. Diurnal variations~~**Figure 1** ~~report the average levels as a filled line and the associated 95th confidence interval calculated by bootstrapping the data (n= 200). Outliers (data >99.5th percentile) were removed for computing the diurnal patterns. Hours are given in UTC. LHR traffic movements (bottom-right plot) are reported as arrivals (dotted lines) and departures (solid lines). The offset between the seasons is largely due to daylight saving time (BST = UTC + 1) in the summer data.~~

~~**Figure 3**~~. Statistics of size distribution spectra for particle number (red) and volume (blue) concentrations categorised by sampling periods and time of the day (daytime= 7am-7pm and nighttime=7pm- 7am local time). For the particle number spectra, solid lines represent the median concentrations, while shaded areas report the 1st-3rd quartile intervals~~.~~ (interquartile range, IQR). For the particle volume spectra, only medians are reported (dotted lines).

**Figure 2.** Diurnal patterns of PNC, LHR traffic, solar irradiance and eBC. Plots report the average levels as a filled line and the associated 95th confidence interval calculated by bootstrapping the data (n= 200). Outliers (data >99.5th percentile) were removed for computing the diurnal patterns. Hours are given in UTC. LHR traffic movements (bottom right plot) are reported as arrivals (dotted lines) and departures (solid lines). The offset between the seasons is largely due to daylight saving time (BST = UTC + 1) in the summer data.~~**Figure 4**~~ The diurnal patterns of all the measured variables in reported in Figure SI~~X~~4.
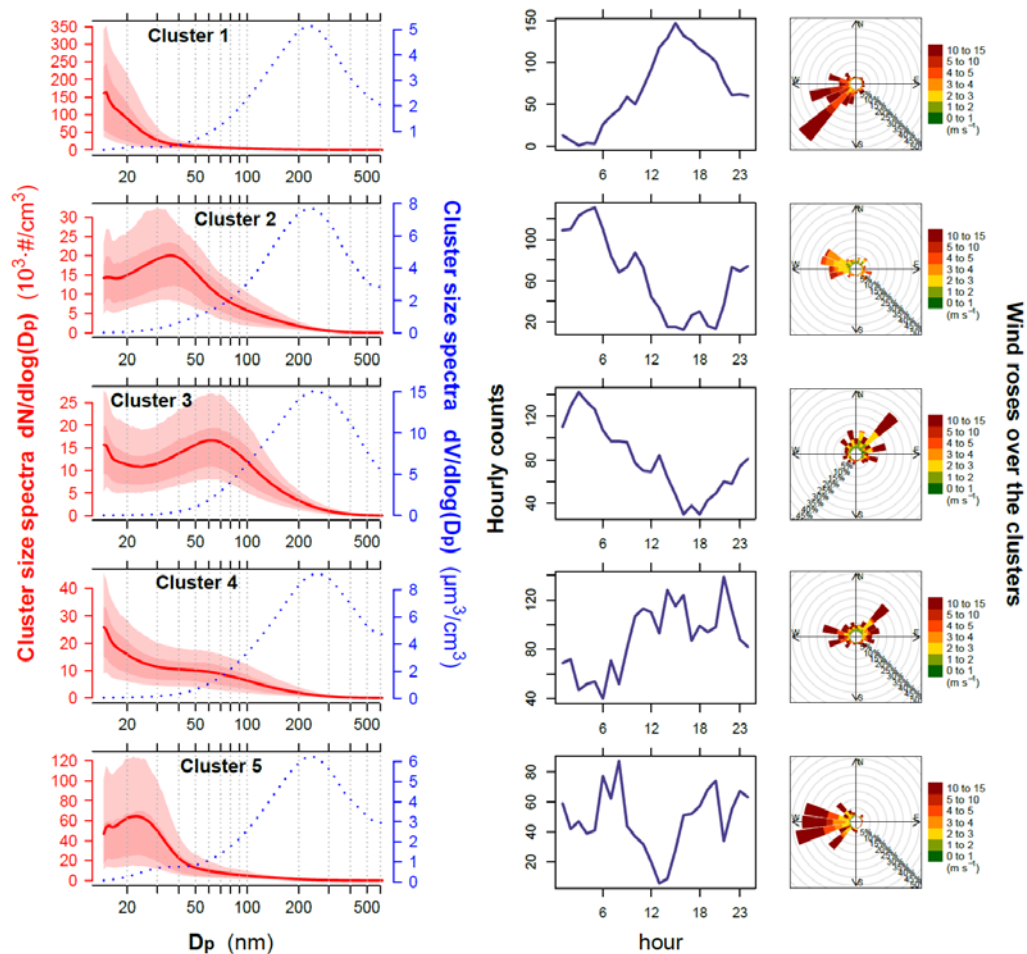
**Figure 3.** Results of cluster analysis for the warm season data. Average cluster PNSD spectra (left) are reported as solid red lines along with: (i) their 10th, 25th, 75th and 90th percentile spectrum as shaded areas; (ii) the volume size distributions (dotted blue line); (iii) the hourly counts and (iv) the wind roses associated with each cluster.

**Figure 4.** Results of cluster analysis for the cold season data. Average cluster PNSD spectra (left) are reported as solid red lines along with: (i) their 10th, 25th, 75th and 90th percentile spectrum as shaded areas; (ii) the volume size distributions (dotted blue line); (iii) the hourly counts and (iv) the wind roses associated with each cluster.

**Figure 5.**

**Figure 5.** Results of cluster analysis for the cold season data. Average cluster PNSD spectra (left) are reported as solid red lines along with: (i) their 10th, 25th, 75th and 90th percentile spectrum as shaded areas; (ii) the volume size distributions (dotted blue line); (iii) the hourly counts and (iv) the wind roses associated with each cluster.

**Figure 6.** Results of PMF analysis for the warm season data. Factor profiles are reported on the left as: (i) number concentration in solid red lines; (ii) their DISP ranges in shaded red areas; (iii) volume concentrations in dotted blue lines; (iv) explained variation in dashed grey lines. The plots on the centre report the normalised daily patterns calculated on the hourly-averaged factor contributions along with their 95th confidence intervals (n=200 bootstrap). The plots on the right show the polar plot analysis (normalised average factor contributions). SA=secondary aerosol.

**Figure 76.** Results of PMF analysis for the cold season data. Factor profiles are reported on the left as: (i) number concentration in solid red lines; (ii) their DISP ranges in shaded red areas; (iii) volume concentrations in dotted blue lines; (iv) explained variation in dashed grey lines. The plots on the centre report the normalised daily patterns calculated on the hourly-averaged factor contributions along with their 95th confidence intervals (n=200 bootstrap). The plots on the right show the polar plot analysis (normalised average factor contributions). SA=secondary aerosol.

**Figure 7.** CWT maps of the secondary aerosol-related factors for both the seasons. Map scales refer to the average factor contributions to the total variable (PNC).

**Figure 8.** CWT maps of the secondary aerosol-related factors for both the seasons. Map scales refer to the average factor contributions to the total variable (PNC).

**Figure 9.** Comparison of k-means and PMF for the warm (upper plots) and cold (bottom plots) seasons. Boxplot statistics: lines= medians, crosses= arithmetic means, boxes= 25th-75th percentile ranges, whiskers= ±1.5*inter-quartile ranges.

**Figure 109.** Analysis of the regional nucleation episode occurring on September 7th. The selected period is from 7 September  midnight to 8 September 4 pm. The plots represent (from upper to the bottom): (a) contour plots of SMPS data; (b) Concentrations of some measured species (Nucl= particles in the nucleation range 14-30 nm; Ait= particles in the Aitken Nuclei range 30-100 nm; Acc= particles in the accumulation range >100 nm; mass of PM2.5); (c) Source contributions from PMF for the Factors 1, 2, 3 and 4; (d) hourly counts of number of clusters. The arrows in the (b) and (c) plots show the wind direction (arrow direction) and speed (proportional to arrow length).

**Figure 11.** Backward air mass trajectories during the nucleation event. Dots indicate 24 h step times

2400 **Table 1**. Summary of PMF results for both seasons.

2401

| Factor number and interpretation | Particle Number Concentration | | Particle Volume Concentration | |
|---|---|---|---|---|
| **Warm season** (Aug-Sep 2014) | No. modes[a] (peak ranges[b]) | Percent contribution (DISP range) | No. modes[a] (peak ranges[b]) | Percent contribution |
| **Factor 1: Airport** | 1 (<20 nm) | 31.6 (30.8–36.2) | 2 (60–160 nm; <25 nm) | 1.2 |
| **Factor 2: Fresh road traffic** | 1 (20–35 nm) | 27.9 (24.7–30.2) | 2 (22–45 nm; 140–220 nm) | 1.7 |
| **Factor 3: Aged road traffic** | 1 (30–60 nm) | 18.9 (16.6–21.1) | 2 (40–100 nm; 250–450 nm) | 5.6 |
| **Factor 4: Urban accumulation** | 1 (50–150 nm) | 14.4 (13.8–18) | 1 (80–250 nm) | 33.2 |
| **Factor 5: Mixed SA[c]** | 1 (110–250 nm) | 5.2 (3.6–6.9) | 1 (160–350 nm) | 37.4 |
| **Factor 6: Inorganic SA** | 2 (55–120 nm; 230–400 nm) | 2.1 (1.1–3.5) | 2 (260–500 nm; 75–140 nm) | 20.8 |
| **Cold season** (Dec 2014-Jan 2015) | | | | |
| **Factor 1: Airport** | 1 (<20 nm) | 33.1 (31.7–34.8) | 2 (160–350 nm; 15–25 nm) | 1.7 |
| **Factor 2: Fresh road traffic** | 1 (18–35 nm) | 35.2 (33.4–36.9) | 2 (22–45 nm; 150–300 nm) | 3.1 |
| **Factor 3: Aged road traffic** | 1 (28–60 nm) | 18.9 (17.9–19.7) | 2 (40–150 nm; 330–450 nm) | 8.7 |
| **Factor 4: Urban accumulation** | 1 (55–170 nm) | 7.6 (7.3–8.3) | 1 (100–250 nm) | 32.5 |
| **Factor 5: Mixed SA** | 2 (130–280 nm, <17 nm) | 2.3 (2.1–3.3) | 1 (170–400 nm) | 30.8 |
| **Factor 6: Inorganic SA** | 3 (17–28 nm; 55–100 nm, 250–400 nm) | 2.9 (2.4–3.9) | 2 (280–550 nm; 90–140 nm) | 23.3 |

(a) Only modes above the DISP ranges are shown; (b) Range endpoints are taken at approx. half the mode height; (c) SA = secondary aerosol.

2402

Table 2. Results of Pearson's correlation analysis among extracted factor contributions and other measured variables recorded at different time resolutions. Only correlations significant at $p<0.05$ are reported, strong correlations ($\rho>|0.6|$) are highlighted in bold.

| | Warm period | | | | | |
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 4** | **Factor 5** | **Factor 6** |
| **Variables** | Airport | Fresh road traffic | Aged road traffic | Urban accumulation | Mixed SA | Inorganic SA |
|---|---|---|---|---|---|---|
| *Weather parameters (1 h-resolution time)* | | | | | | |
| **Solar irr.** | 0.12 | -0.15 | -0.24 | -0.26 | -0.24 | -0.28 |
| **Air temp.** | 0.25 | -0.21 | -0.37 | -0.1 | 0.1 | |
| **RH** | | 0.1 | 0.32 | 0.22 | 0.26 | 0.33 |
| **Wind speed** | 0.38 | | -0.47 | **-0.64** | -0.45 | -0.49 |
| *5 min-resolution time* | | | | | | |
| **Factor 1** | – | | | | | |
| **Factor 2** | 0.46 | – | | | | |
| **Factor 3** | 0.03 | 0.28 | – | | | |
| **Factor 4** | -0.17 | -0.04 | 0.47 | – | | |
| **Factor 5** | -0.15 | -0.06 | 0.21 | 0.56 | – | |
| **Factor 6** | -0.17 | -0.14 | 0.15 | 0.56 | **0.75** | – |
| **eBC** | -0.1 | -0.03 | 0.3233 | **0.6162** | 0.5452 | 0.5553 |
| **Delta-C** | | | -0.0613 | -0.0907 | -0.12 | -0.1306 |
| *1 h-resolution time* | | | | | | |
| **NO** | | | 0.43 | **0.6** | 0.32 | 0.33 |
| **NO$_2$** | | 0.18 | **0.61** | **0.76** | 0.52 | 0.52 |
| **NO$_x$** | | 0.11 | 0.58 | **0.77** | 0.48 | 0.48 |
| **O$_3$** | 0.14 | -0.19 | -0.57 | -0.54 | -0.37 | -0.43 |
| **PM$_{2.5}$** | -0.23 | -0.24 | 0.13 | **0.61** | **0.63** | **0.77** |
| **NVPM$_{2.5}$** | -0.22 | -0.22 | 0.17 | **0.62** | **0.61** | **0.75** |
| **VPM$_{2.5}$** | -0.17 | -0.24 | | 0.42 | 0.54 | **0.65** |
| *1 day-resolution time PM$_{2.5}$-bound species* | | | | | | |
| **OC** | | | | **0.84** | **0.74** | **0.83** |
| **EC** | -0.47 | -0.54 | | **0.75** | 0.51 | **0.67** |
| **TC** | -0.45 | -0.44 | | **0.85** | **0.69** | **0.82** |
| **Chloride** | | | | | | |
| **Nitrate** | | -0.45 | | | **0.83** | **0.85** |
| **Sulphate** | | -0.57 | | **0.75** | 0.5 | **0.67** |
| **Oxalate** | | -0.47 | | 0.59 | **0.89** | **0.93** |
| **Sodium** | | | | | | |
| **Ammonium** | -0.44 | -0.52 | | 0.57 | 0.54 | **0.71** |
| **Potassium** | | -0.47 | | 0.46 | 0.5 | **0.66** |
| **Magnesium** | 0.5 | | | -0.53 | | |
| **Calcium** | | | | | | |

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The numbers in eBC and Delta-C rows show tracked-change edits (struck-through old values with new values).

Table 2. Continued.

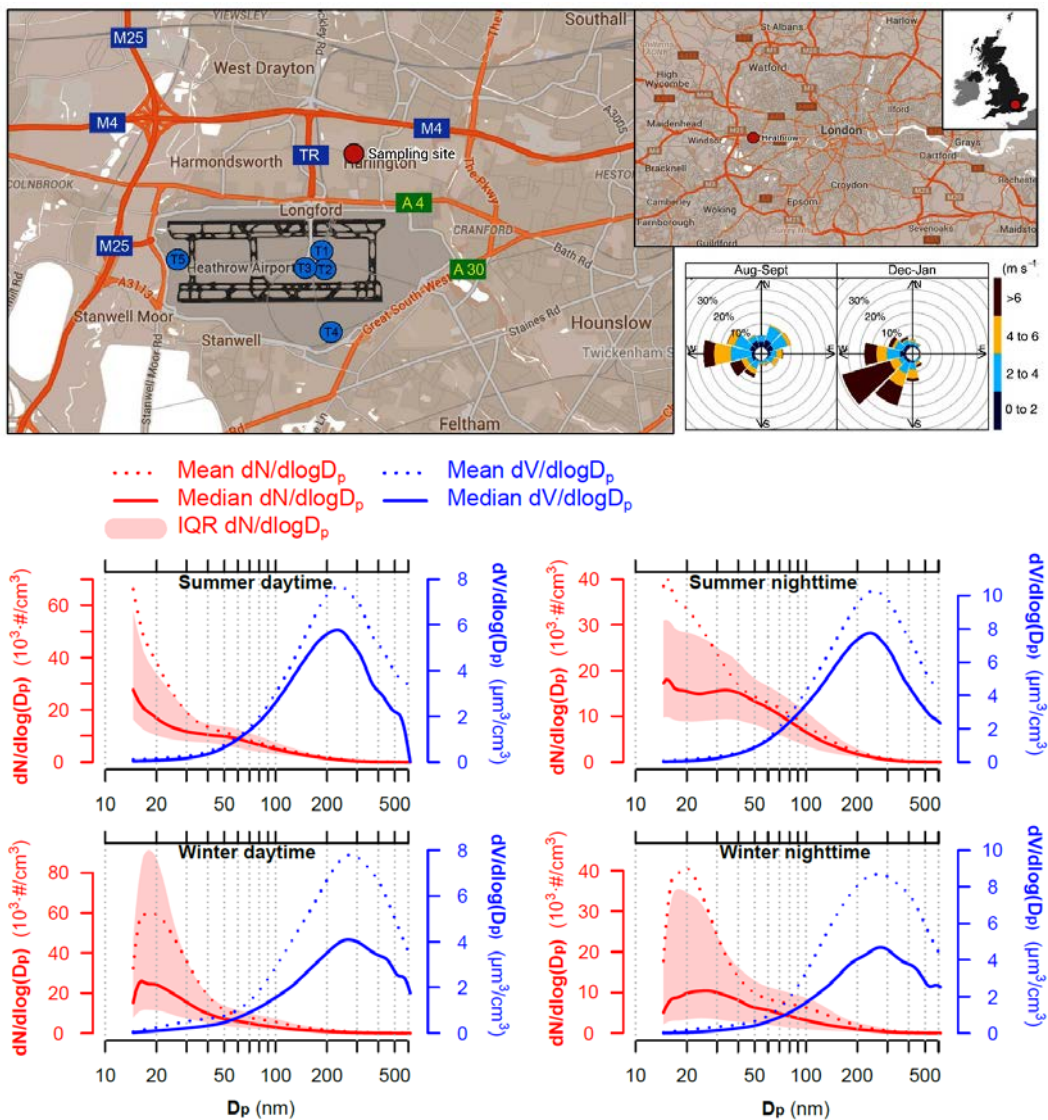| Variables | Factor 1 Airport | Factor 2 Fresh road traffic | Factor 3 Aged road traffic | Factor 4 Urban accumulation | Factor 5 Mixed SA | Factor 6 Inorganic SA |
|---|---|---|---|---|---|---|
| **Cold period** | | | | | | |
| *Weather parameters (1 h-resolution time)* | | | | | | |
| **Solar irr.** | | | | -0.11 | | |
| **Air temp.** | 0.38 | | -0.43 | **-0.67** | -0.5 | -0.59 |
| **RH** | | | 0.23 | 0.38 | 0.46 | 0.46 |
| **Wind speed** | 0.3 | | -0.49 | **-0.67** | -0.54 | **-0.61** |
| *5 min-resolution time* | | | | | | |
| **Factor 1** | – | | | | | |
| **Factor 2** | 0.55 | – | | | | |
| **Factor 3** | 0.24 | 0.54 | – | | | |
| **Factor 4** | -0.11 | 0.08 | 0.53 | – | | |
| **Factor 5** | -0.05 | 0.15 | 0.38 | **0.65** | – | |
| **Factor 6** | -0.09 | 0.08 | 0.39 | **0.7** | **0.81** | – |
| **eBC** | | 0.~~19~~16 | **0.~~54~~52** | **0.~~75~~77** | **0.~~57~~60** | **0.~~61~~63** |
| **Delta-C** | | | 0.~~1~~35 | **0.~~21~~62** | 0.~~22~~55 | 0.~~19~~52 |
| *1 h-resolution time* | | | | | | |
| **NO** | -0.14 | | 0.51 | **0.81** | **0.62** | **0.63** |
| **NO$_2$** | 0.13 | 0.42 | **0.81** | **0.82** | **0.61** | **0.66** |
| **NO$_x$** | | 0.17 | **0.63** | **0.85** | **0.64** | **0.68** |
| **O$_3$** | | -0.29 | **-0.71** | **-0.78** | **-0.65** | **-0.7** |
| **PM$_{2.5}$** | -0.1 | 0.16 | 0.53 | **0.82** | **0.88** | **0.88** |
| **NVPM$_{2.5}$** | -0.11 | 0.16 | 0.53 | **0.82** | **0.85** | **0.85** |
| **VPM$_{2.5}$** | | | 0.19 | 0.39 | 0.49 | 0.48 |
| *1 day-resolution time PM$_{2.5}$-bound species* | | | | | | |
| **OC** | | | **0.79** | **0.79** | **0.76** | **0.8** |
| **EC** | | | **0.83** | **0.8** | **0.64** | **0.66** |
| **TC** | | | **0.81** | **0.8** | **0.73** | **0.77** |
| **Chloride** | | | | 0.58 | **0.82** | **0.85** |
| **Nitrate** | | **0.63** | **0.73** | **0.88** | **0.93** | **0.9** |
| **Sulphate** | | | | | **0.92** | **0.88** |
| **Oxalate** | | | | | **0.87** | **0.81** |
| **Sodium** | | -0.58 | **-0.74** | **-0.64** | | |
| **Ammonium** | | | **0.63** | **0.78** | **0.99** | **0.97** |
| **Potassium** | | | | **0.71** | **0.98** | **0.97** |
| **Magnesium** | | | | | | |
| **Calcium** | | | | | | |

81

**Figure 1.** ~~Map of LHR and sampling site (left) and map of the Greater London area (upper right).~~
~~Wind roses calculated over the two sampling periods are also provided (bottom right). The location~~
~~of some main potential sources is also highlighted: T1, T2, T3, T4 and T5 are the Heathrow~~
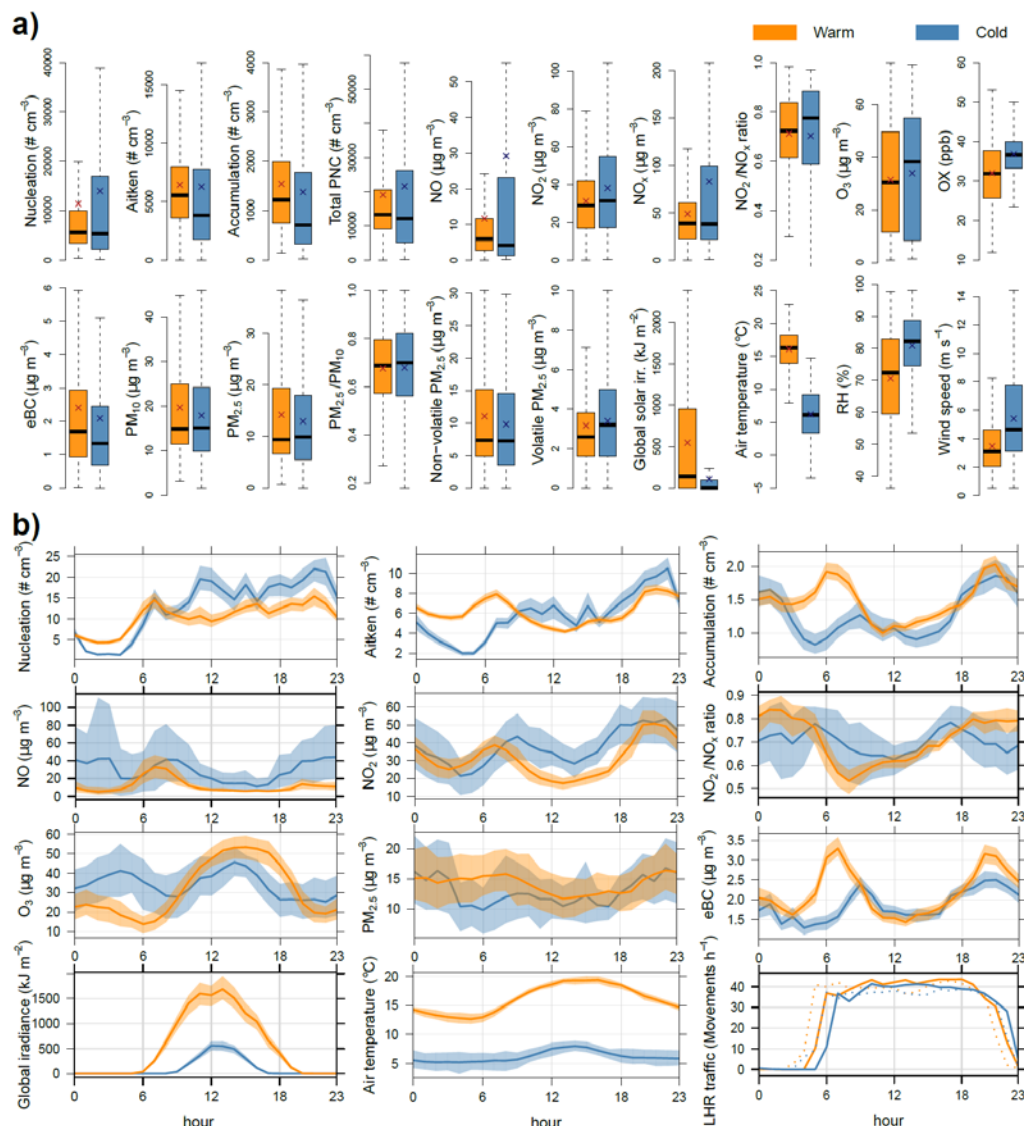~~terminals; TR= Tunnel Rd.~~

**Figure 2.** Boxplots (a) and diurnal patterns (b) of the most important measured variables (and derived variables) during the two sampling periods. All valid data are used for computing boxplot statistics: Boxplot lines= medians, crosses= arithmetic means, boxes= 25th-75th percentile ranges, whiskers= ±1.5*inter-quartile ranges. Diurnal variations report the average levels as a filled line and the associated 95th confidence interval calculated by bootstrapping the data (n= 200). Outliers (data >99.5th percentile) were removed for computing the diurnal patterns. Hours are given in UTC. LHR traffic movements (bottom right plot) are reported as arrivals (dotted lines) and departures (solid lines). The offset between the seasons is largely due to daylight saving time (BST = UTC + 1) in the summer data.

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2432  **Figure 3.** Statistics of size distribution spectra for particle number (red) and volume (blue)
2433  concentrations categorised by sampling periods and time of the day (daytime= 7am-7pm and
2434  nighttime=7pm- 7am local time). For the particle number spectra, solid lines represent the median
2435  concentrations, while shaded areas report the 1st-3rd quartile intervals. (interquartile range, IQR).
2436  For the particle volume spectra, only medians are reported (dotted lines).

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2440  **Figure 2.** Diurnal patterns of PNC, LHR traffic, solar irradiance and eBC. Plots report the average
2441  levels as a filled line and the associated 95th confidence interval calculated by bootstrapping the
2442  data (n= 200). Outliers (data >99.5th percentile) were removed for computing the diurnal patterns.
2443  Hours are given in UTC. LHR traffic movements (bottom right plot) are reported as arrivals (dotted
2444  lines) and departures (solid lines). The offset between the seasons is largely due to daylight saving

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2447 The diurnal patterns of all the measured variables in reported in Figure SIX.
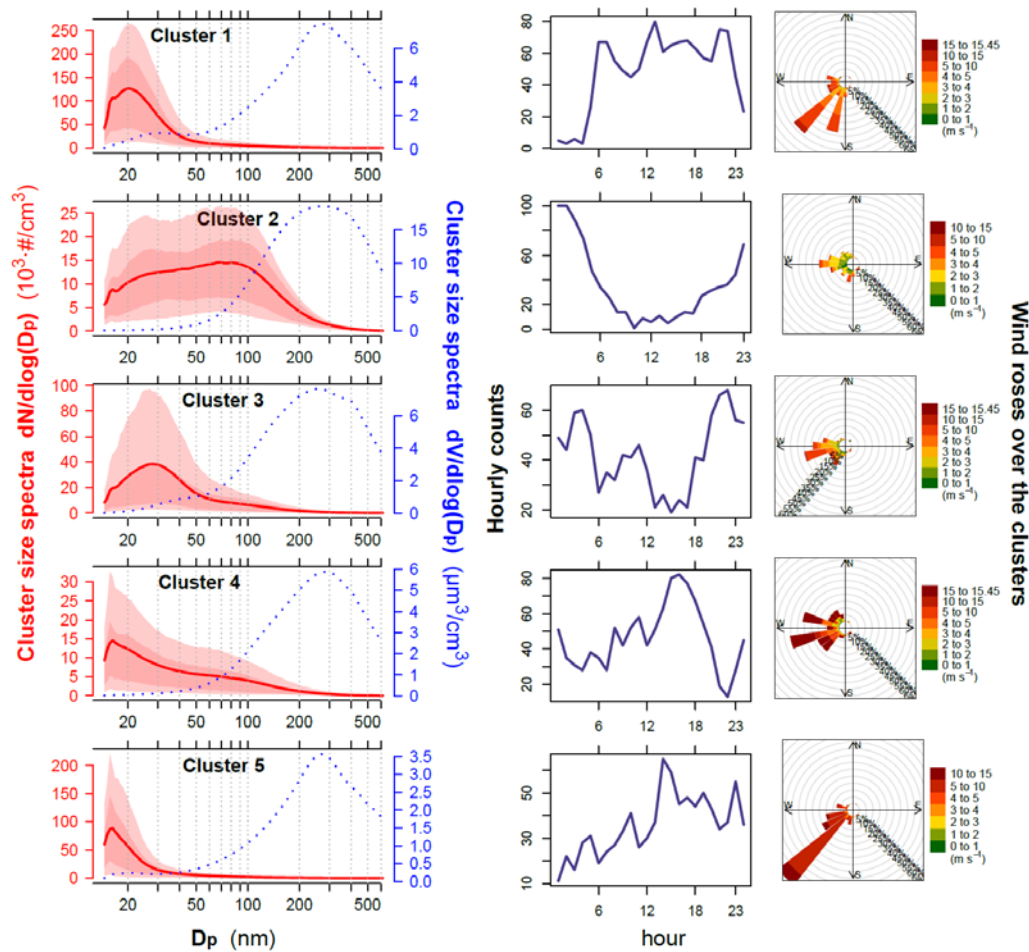
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**Figure 3.**~~Figure 4.~~ Results of cluster analysis for the warm season data. Average cluster PNSD
spectra (left) are reported as solid red lines along with: (i) their 10th, 25th, 75th and 90th percentile
spectrum as shaded areas; (ii) the volume size distributions (dotted blue line); (iii) the hourly counts
and (iv) the wind roses associated with each cluster.

2454

**Figure 54.** Results of cluster analysis for the cold season data. Average cluster PNSD spectra (left) are reported as solid red lines along with: (i) their 10th, 25th, 75th and 90th percentile spectrum as shaded areas; (ii) the volume size distributions (dotted blue line); (iii) the hourly counts and (iv) the wind roses associated with each cluster.
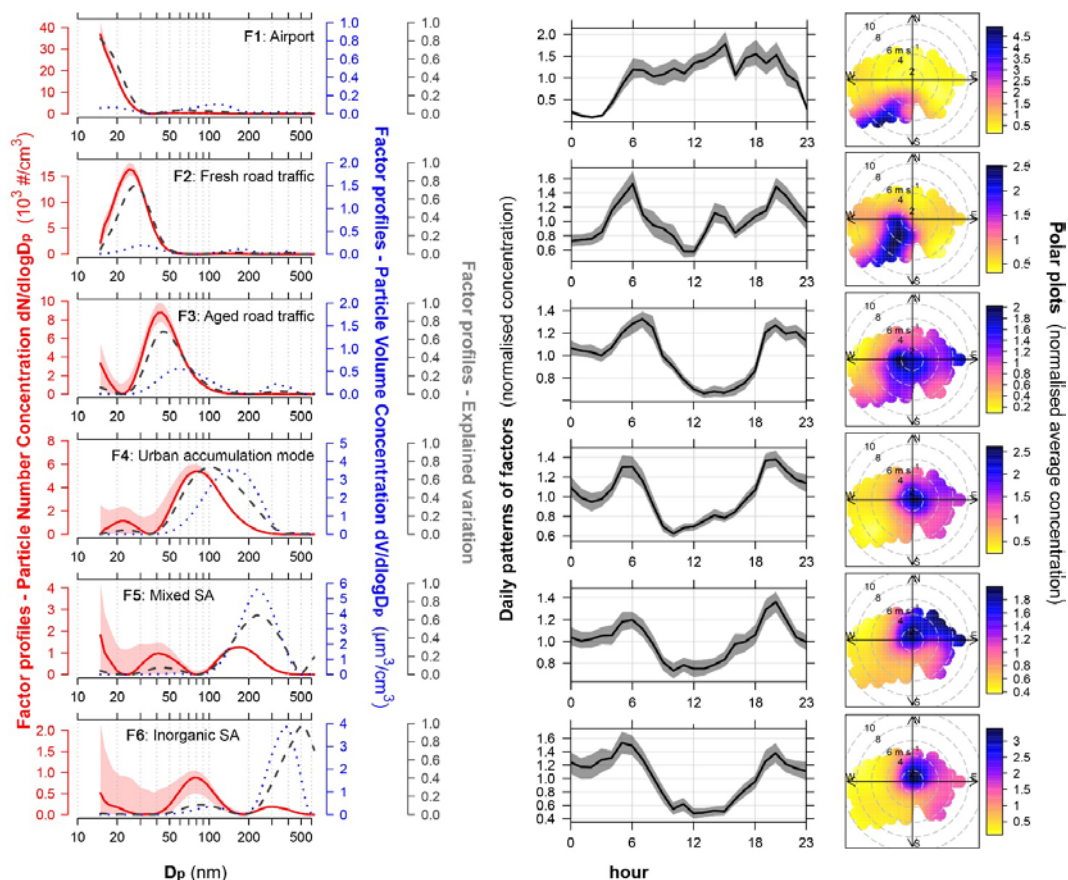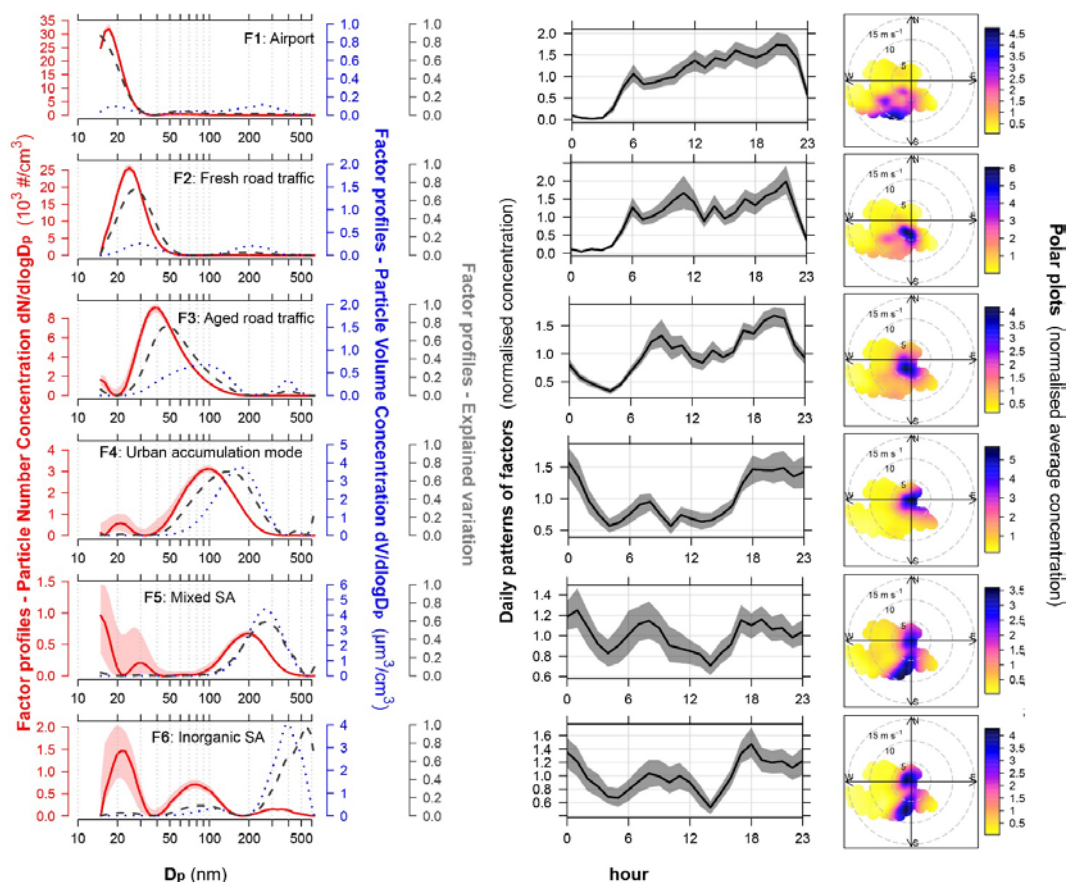
**Figure 65.** Results of PMF analysis for the warm season data. Factor profiles are reported on the left as: (i) number concentration in solid red lines; (ii) their DISP ranges in shaded red areas; (iii) volume concentrations in dotted blue lines; (iv) explained variation in dashed grey lines. The plots on the centre report the normalised daily patterns calculated on the hourly-averaged factor contributions along with their 95th confidence intervals (n=200 bootstrap). The plots on the right show the polar plot analysis (normalised average factor contributions). SA=secondary aerosol.
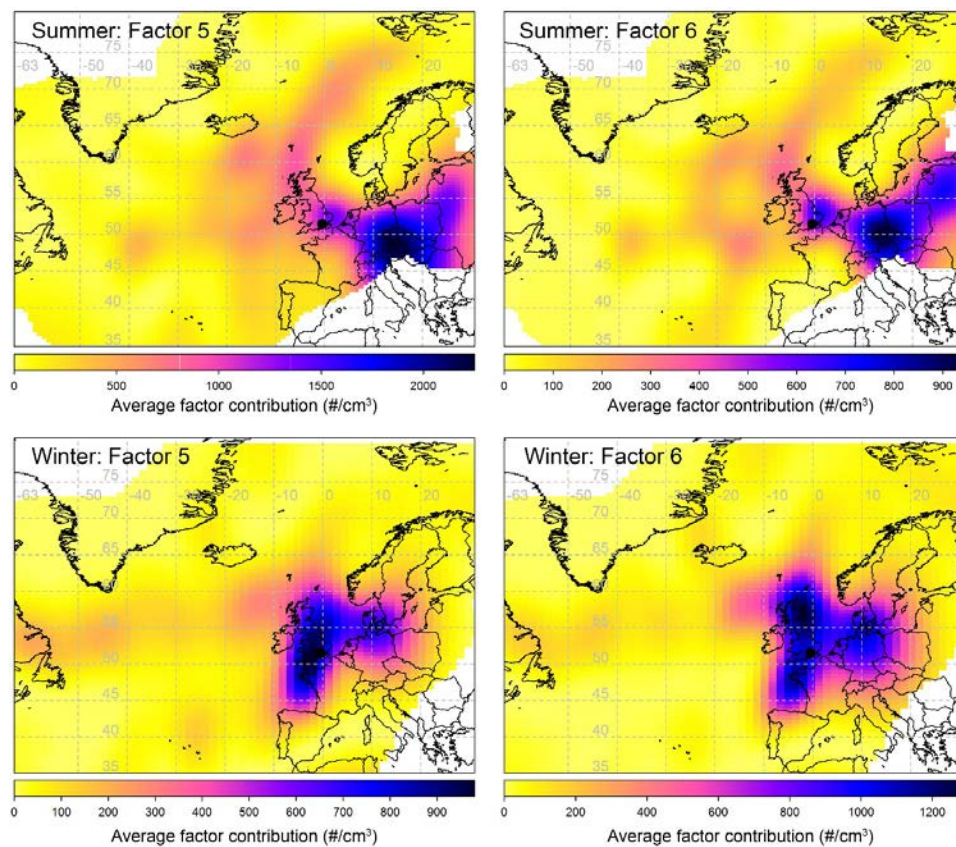
**Figure 76.** Results of PMF analysis for the cold season data. Factor profiles are reported on the left as: (i) number concentration in solid red lines; (ii) their DISP ranges in shaded red areas; (iii) volume concentrations in dotted blue lines; (iv) explained variation in dashed grey lines. The plots on the centre report the normalised daily patterns calculated on the hourly-averaged factor contributions along with their 95th confidence intervals (n=200 bootstrap). The plots on the right show the polar plot analysis (normalised average factor contributions). SA=secondary aerosol.
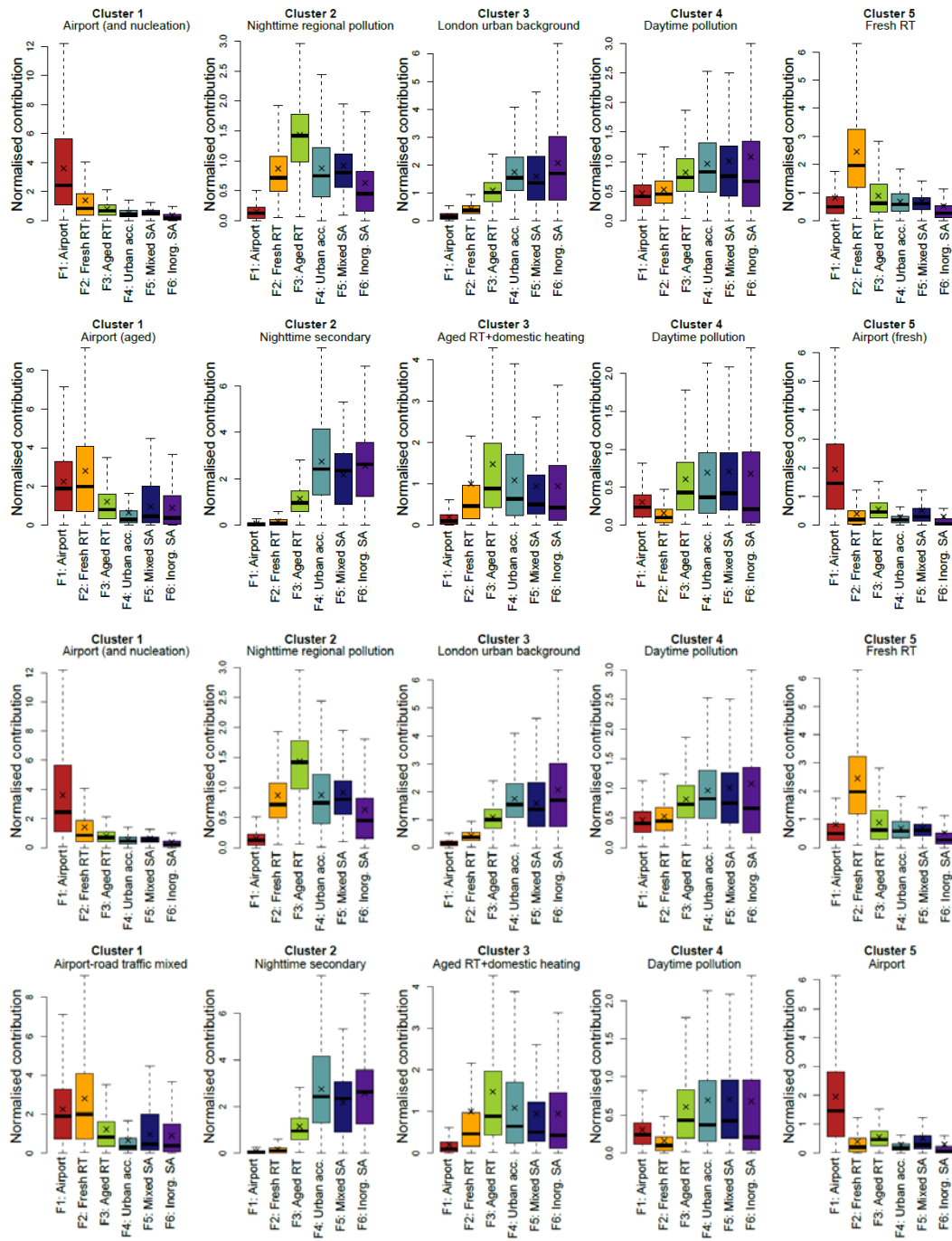
**Figure 87.** CWT maps of the secondary aerosol-related factors for both the seasons. Map scales refer to the average factor contributions to the total variable (PNC).

**Figure 98.** Comparison of k-means and PMF for the warm (upper plots) and cold (bottom plots) seasons. Boxplot statistics: lines= medians, crosses= arithmetic means, boxes= 25th-75th percentile ranges, whiskers= ±1.5*inter-quartile ranges.
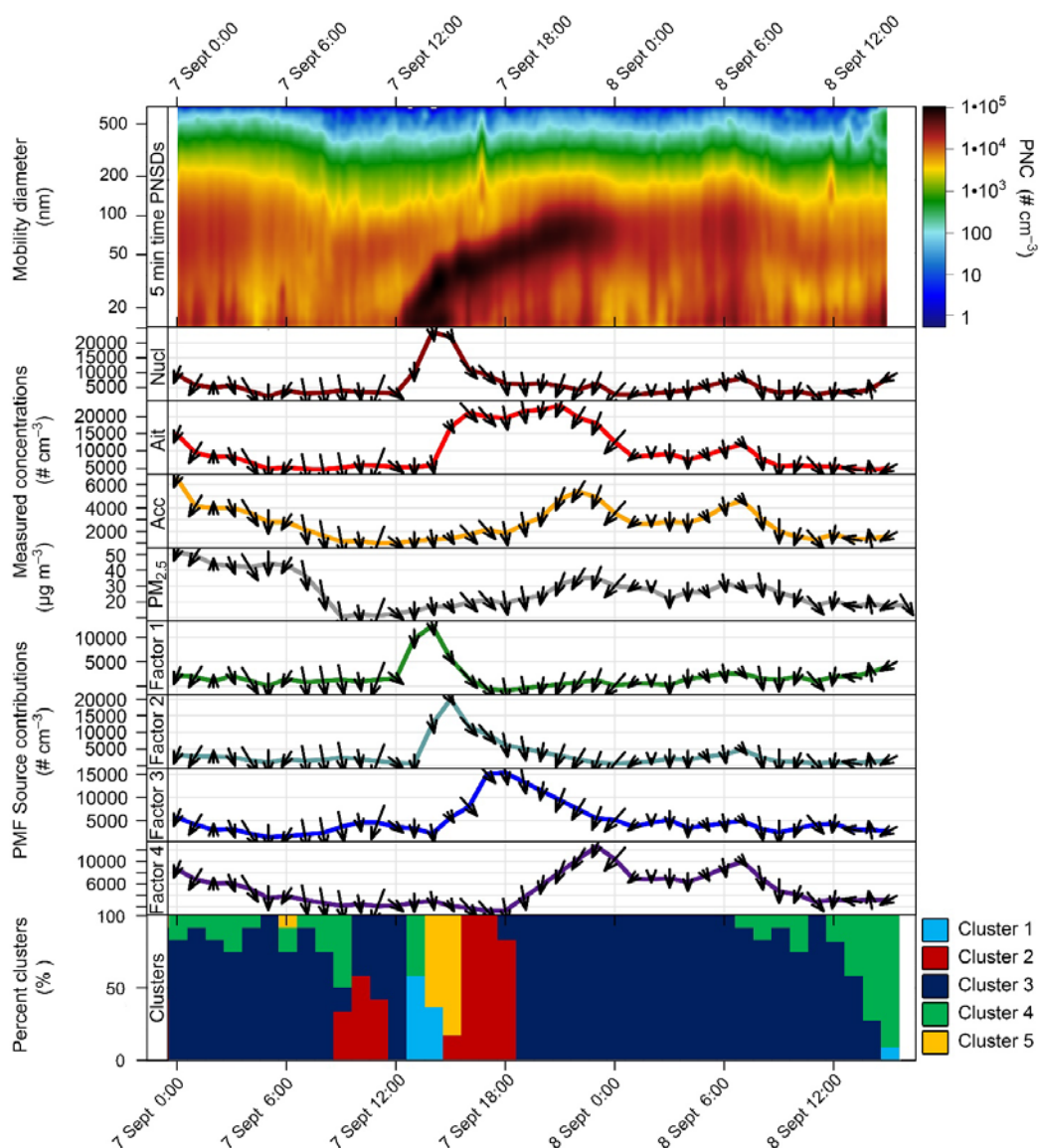
**Figure 109.** Analysis of the regional nucleation episode occurring on September 7th. The selected period is from 7 September midnight to 8 September 4 pm. The plots represent (from upper to the bottom): (a) contour plots of SMPS data; (b) Concentrations of some measured species (Nucl= particles in the nucleation range 14-30 nm; Ait= particles in the Aitken Nuclei range 30-100 nm; Acc= particles in the accumulation range >100 nm; mass of PM$_{2.5}$); (c) Source contributions from PMF for the Factors 1, 2, 3 and 4; (d) hourly counts of number of clusters. The arrows in the (b) and (c) plots show the wind direction (arrow direction) and speed (proportional to arrow length).
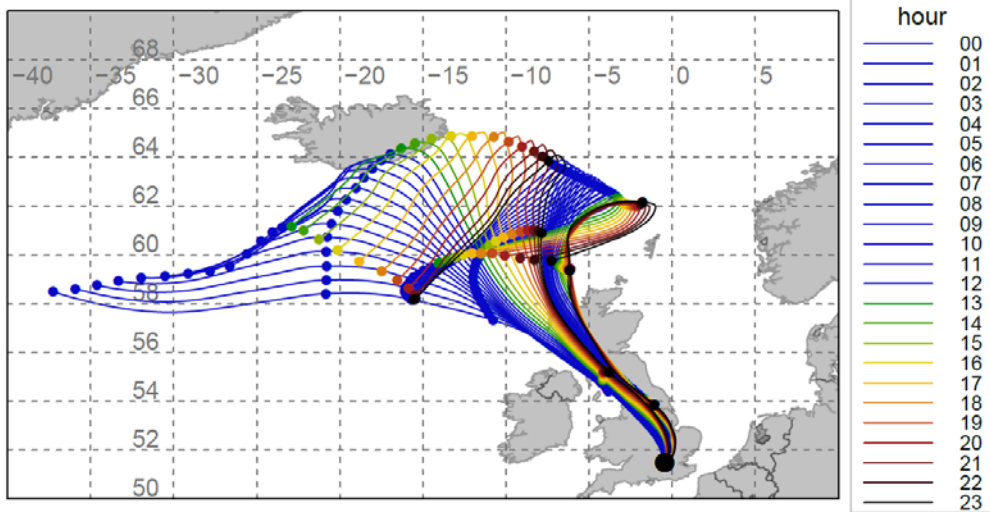
7 September 2014

**Figure 11.** Backward air mass trajectories during the nucleation event. Dots indicate 24 h step times