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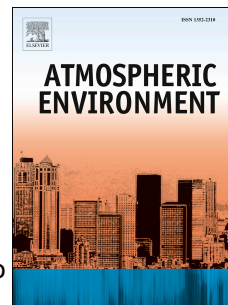
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Aircraft observations of the lower troposphere above a megacity: alkyl nitrate and ozone chemistry

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1 **Aircraft observations of the lower troposphere above a** 2 **megacity: alkyl nitrate and ozone chemistry**

3

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28

29 **Abstract**

30 Within the framework of the RONOCO (ROle of Nighttime chemistry in controlling the Oxidising
31 Capacity of the atmOsphere) campaign a daytime flight over the metropolitan area of London were
32 carried out to study the nitrogen oxide chemistry and its role in the production and loss of ozone
33 (O_3) and alkyl and multifunctional nitrate (ΣANs). The FAAM BAe-146 aircraft, used for these
34 observations, was equipped with instruments to measure the most relevant compounds that control
35 the lower troposphere chemistry, including O_3 , NO , NO_2 , NO_3 , N_2O_5 , HNO_3 , peroxy nitrates
36 (ΣPNs), ΣANs , OH , and HO_2 . In the London's flight a strong ozone titration process was observed
37 when flying above Reading (downwind of London) and when intercepting the London plume. The
38 coupled cycles of NO_x and HO_x can have different terminations forming ΣPNs , ΣANs , HNO_3 or
39 peroxides (H_2O_2 , $ROOH$) altering the O_3 production. In the observations reported here, we found
40 that a strong ozone titration ($\Delta O_3 = -16$ ppb), due to a rapid increase of NO_x ($\Delta NO_x = 27$ ppb),
41 corresponds also to a high increase of ΣANs concentrations ($\Delta \Sigma ANs = 3$ ppb), and quite stable
42 concentrations of HNO_3 and ΣPNs . Unexpectedly, compared with other megacities, the production
43 of ΣANs is similar to that of O_x ($O_3 + NO_2$), suggesting that in the London plume, at least during
44 these observations, the formation of ΣANs effectively removes active NO_x and hence reduces the
45 amount of O_3 production. In fact, we found that the ratio between the ozone production and the
46 alkyl nitrates production (observed) approximate the unity; on the contrary the calculated ratio is 7.
47 In order to explain this discrepancy, we made sensitivity tests changing the alkyl nitrates branching
48 ratio for some VOCs and we investigated the impact of the unmeasured VOCs during the flight,
49 founding that the calculated ratio decreases from 7 to 2 and that, in this condition, the major

50 contribution to the ΣANs production is given by Alkanes. Observations and analysis reported here
51 suggest that in the London plume the high NO_x emissions and the chemistry of some VOCs (mainly
52 Alkanes) produce high concentrations of ΣANs competing against the local ozone production.

53

54 **Highlights**

- 55 • Daytime chemical and aerosol composition have been measured around London with an
56 aircraft
- 57 • Unexpected high production of alkyl nitrate comparable to that of ozone
- 58 • The low O_3 production put the chemistry above London quite different compared with other
59 megacities

60

61 **Keywords**

62 Ozone production; alkyl nitrates production; tropospheric chemistry; urban pollution; aircraft;
63 London.

64

65 **1. Introduction**

66 NO_x ($NO_x = NO + NO_2$), produced principally as NO by human activity (transport, industrial
67 combustion, etc.), and O_3 are significant tropospheric pollutants that can have negative impact on
68 the vegetation, ecosystems and human health (e.g. European Environment Agency (EEA), 2005). In
69 recent years the scientific community has paid considerable attention to the study of the chemical
70 and physical mechanisms that control the chemistry of nitrogen compounds in the troposphere,
71 focusing in detail on NO_x and the total reactive oxidized nitrogen species, NO_y ($NO_y = NO_x + NO_z$,
72 where $NO_z = RO_2NO_2 + RONO_2 + HNO_3 + HONO + 2N_2O_5 + NO_3$). Some of the NO_z compounds
73 are a sink for NO_x (for example HNO_3), whereas other are a temporary reservoirs of NO_x in the
74 troposphere and therefore their formation can enhance ozone production if the NO_x is released

75 downwind into a low NO_x environment (e.g. Jacob et al, 1999; Day et al., 2002). In the troposphere,
 76 the termination of coupled cycles of NO_x and HO_x ($HO_x = OH + HO_2$) has been studied in detail in
 77 recent years due to their impact on peroxy nitrates (ΣPNs), alkyl and multifunctional nitrates
 78 (ΣANs) and O_3 formation. When a hydrocarbon (RH) is oxidised by OH , a peroxy radical (RO_2) is
 79 formed, which can react with NO forming either an alkyl nitrate (R2) or alkoxy radical RO (R3), the
 80 latter lead the production of NO_2 and therefore, after its photolysis, produces two molecules of O_3 .

81



82

83 The urban environments are very interesting and well investigated from the point of view of air
 84 quality because of intense human activities that characterize these areas. Different campaigns have
 85 been carried out in the London metropolitan area. The results of the REPARTEE (REgents PARK
 86 and Tower Environmental Experiment) project have been presented by Harrison et al. (2012). They
 87 showed the chemical and physical mechanisms controlling the London atmosphere and introduced a
 88 history of London air quality problems: for example, in consequence of the Great Smog in 1952,
 89 more than 4000 excess deaths have been estimated. In contrast to what was observed in other
 90 important megacities, such as Mexico City or Los Angeles, Charron et al. (2007) found that a large
 91 fraction of the particulate matter (PM10) measured in London derived from regional backgrounds.
 92 This result suggests that in depth study of the atmospheric composition in urban areas and the

93 regional background around London is therefore important (Harrison et al., 2012). During the
94 REPARTEE study, a collaboration with the CityFlux experiment (Langford et al., 2010) was
95 established to carry out measurements of Volatile Organic Compounds (*VOCs*) and aerosols fluxes
96 and chemical compositions in different urban areas of London. They found that the traffic emissions
97 contribute for more than 70% of the aromatic compounds and in general are the principal source of
98 *VOCs* in the London plumes. The study of the *VOCs* fluxes and concentrations by Langford et al.
99 (2010) shows that their observations are in agreement with the measurements of the UK NAEI
100 (National Atmospheric Emission Inventory) for aromatic *VOCs*. In contrast for the species emitted
101 by several and diffuse area sources (as acetaldehyde or acetone, produced also by paints, solvents
102 etc.) the emission inventory underestimates the observations of Langford et al. (2010).

103 McMeeking et al. (2012) presented the results of their measurements during the EM25 (Emissions
104 around the M25 motorway) campaign (June 2009) in London. They identified the London plume
105 with respect to the regional background, measuring different concentrations of the most significant
106 compounds emitted in the urban area (NO_x , CO , some *VOCs* and black carbon (*BC*)) flying within
107 or outside the city plume and characterized the two air masses by composition and age. They
108 studied the aerosol mass distribution, finding little difference between the urban plume and the
109 regional aerosol. The two case studies reported in their work show that the London plume advected
110 west for the flight on 23 June 2009, characterized by easterly flow, and remained over London for
111 the more stagnant 22 June 2009 flight. Moreover, during the flight of 23 June the NO_x concentration
112 measured above Reading was significantly high, reach the maximum value of about 30 ppb. As a
113 consequence of the high NO_x concentration over Reading, they reported a decreasing ratio between
114 O_3 and NO_x as low as close to zero indicating a significant ozone titration processes in the London
115 plumes.

116 As previously illustrated, an interesting aspect of the tropospheric chemical mechanisms within the
117 urban and suburban environments is the balance between the alkyl nitrates and the ozone production

118 in the NO_x - HO_x coupled cycles (R1-R7 reactions); its implications for the chemical composition of
119 the troposphere have been investigated by several authors in different urban environments. Rosen et
120 al. (2004) measured ΣANs during the Texas Air Quality Study in 2000 (TexAQS-2000) at La Porte
121 and calculated the ratio between the ozone production and the ΣANs production finding slopes of
122 $\Delta O_3/\Delta ANs$ between 29 and 41 that implies a high yield (between 0.065 and 0.047) for alkyl nitrate.
123 Perring et al. (2010) investigated the production of the ΣANs in the Mexico City plume finding that
124 the alkyl nitrates play a significant role in the photochemistry of this urban site since they observed
125 that ΣANs was 10-20% of the NO_y and its formation suppresses peak ozone production rates by
126 about 40% . Farmer et al. (2011) used a model and data observed in Mexico City to point out the
127 role of alkyl nitrates in the photochemistry of the lower troposphere: they showed that ΣANs
128 production can affect the O_3 production. This has implications on the dependence of O_3 production
129 on NO_x and $VOCs$ and therefore on designing air quality control strategies since current chemical
130 mechanisms included in urban and regional air quality models omit details of the alkyl nitrates
131 production.

132 The RONOCO (Role of Nighttime chemistry in controlling the Oxidising Capacity of the
133 Atmosphere) project was carried out to investigate the nocturnal chemistry around the UK during
134 different seasons, with particular attention given to the role of the nitrate radical. In this framework,
135 two airborne campaigns were carried out during July-September 2010 and January 2011. The
136 principal deliverables of the project are: 1) comprehensive measurements of nighttime radicals,
137 their sources and sinks, and aerosol composition in the boundary layer and free troposphere in a
138 range of conditions; 2) quantification of the key processes that control nighttime chemical
139 processes; 3) assessment of the impacts of nighttime chemistry on regional scales; 4) an assessment
140 of the global impacts of nighttime chemistry in the current and future atmospheres (Stone et al.,
141 2013).

142 In this paper we analyse the observations carried out on-board the BAe-146 aircraft during a
143 daytime flight along the M25 motorway around the megacity of London. The flight consists of three
144 runs with a very similar path to follow the M25 motorway. Here the simultaneous measurements of
145 compounds not observed in McMeeking et al. (2012), like ΣPNs , ΣANs and HNO_3 can help a
146 further understanding of the chemistry around London. The main goal is to investigate the role of
147 NO_x and NO_y in the ozone budget of this area.

148

149 2. Instrumental

150

151 The observations that will be presented in this work were carried out aboard the UK BAe 146-301
152 atmospheric research aircraft of the Facility for Airborne Atmospheric Measurements (FAAM).
153 During the RONOCO campaign several instruments were fitted on the BAe-146-301 aircraft, but
154 here only the instruments from which data are used in the analysis are described. NO_2 , ΣPNs and
155 ΣANs were measured using the TD-LIF (Thermal Dissociation – Laser Induced Fluorescence)
156 instrument developed at the University of L'Aquila (Italy). Briefly, the TD-LIF light source is a
157 pulsed YAG-laser (Spectra-Physics, model Navigator I) that emits light at 532 nm with a power of
158 3.8 W, a repetition rate of 15 kHz. The laser beam is steered by two high reflectivity mirrors (99%)
159 before entering the first detection cell through a 5 cm diameter window, and leaves the other side of
160 the cell through another antireflection window. In this configuration the laser radiation is sent
161 sequentially through four cells: after each cell the beam is steered into the subsequent cell using
162 high reflectivity mirrors. The laser power is monitored before and after each cell by four photodiode
163 detectors (UDT55) to compensate the fluorescence counts for the laser power changes. In the first
164 cell is measured directly NO_2 , whereas ΣPNs , ΣANs and HNO_3 are thermally convert into NO_2 and
165 measured as difference between the NO_2 detected by adjacent cells (Day et al., 2002; Di Carlo et al.,
166 2013). The conversion temperatures, in the RONOCO configuration, were 200°C, 400°C and 550°C
167 for ΣPNs , ΣANs and HNO_3 , respectively. Ambient air is sampled through a common inlet (a PFA

168 tube of 120 cm, 6.4 mm OD and 3.8 mm ID) at a flow rate of ~8.4 l/min and, subsequently, it is
169 split into 4 equal flows to pass through four U-shaped quartz tubes (60 cm length, 6 mm OD, 3.8
170 mm ID). The first quartz tube is not heated because goes to the NO_2 cell, whereas the other are
171 heated at the 3 distinct temperatures reported above to measure in the last three distinct cells ΣPNs ,
172 ΣANs and HNO_3 , respectively. The TD-LIF is calibrated using a mixture of high purity zero air and
173 a NIST traceable NO_2 . The detection limits of the TD-LIF, in the RONOCO configuration, are: 9.8
174 pptv, 18.4 pptv, 28.1 pptv and 49.7 pptv (1 s, S/N = 2) for detection of NO_2 by the NO_2 cell, ΣPNs
175 cell, ΣANs cell and HNO_3 cell, respectively. The accuracy depends on the uncertainty of the
176 standards and mass flow controller used for the calibration and in this configuration is 10%, 22%,
177 34% and 46% for NO_2 cell, ΣPNs cell, ΣANs cell and HNO_3 cell, respectively. More information
178 about the TD-LIF system, its controller and the calibration system can be found in Di Carlo et al.
179 (2013) and Dari Salisburgo et al. (2009).

180 The measurements of O_3 and CO were made using a standard TECO 49C UV photometric
181 instrument and an UV fluorescence Aero-Laser AL5002 instrument, respectively (FAAM
182 instruments). Detailed information about the technique and the calibration procedures of those
183 analyzers can be found elsewhere (Hopkins et al., 2011).

184 A chemiluminescent instrument was also used to measure the NO_x (FAAM instrument); in this
185 method ambient NO reacts with O_3 generated by the instrument, to produce electronically excited
186 NO_2 , which relaxes and emits a photon. The concentration of NO is directly measured detecting the
187 chemiluminescence light emitted by the excited NO_2 . Ambient NO_2 is detected after a photolytically
188 conversion (using a blue-light LED, centred at 395 nm) into NO (Sadanaga, et al., 2010).

189 In order to measure *VOCs* concentrations a WAS (Whole Air Sampling) coupled to a GC-FID (Gas
190 Chromatography Flame Ionization Detector) (University of York) instrument was used. The WAS
191 system consists of sixty four silica passivated stainless steel canisters of three litres internal volume
192 (Thames Restek, UK) fitted to the rear hold of the aircraft (Hopkins et al., 2002, 2011).

193 *OH* and *HO₂* were measured by the University of Leeds aircraft FAGE (Fluorescence Assay by Gas
194 Expansion) instrument. The instrument samples ambient air through a pinhole which extends
195 through a window blank in the aircraft, and the gas flows through low-pressure (~1.8 Torr)
196 detection cells for *OH* and *HO₂* in series. *OH* is detected by laser-induced fluorescence
197 spectroscopy, in which the radical is electronically excited by laser light at $\lambda \sim 308$ nm. *HO₂* is
198 detected in the downstream cell following conversion to *OH* with an excess of *NO*. During
199 RONOCO, the detection cell pressure varied from 1.2 Torr at 6 km to 1.9 Torr at sea level. The
200 limits of detection for *OH* and *HO₂* during flight B536 were 1.8×10^6 and 6.9×10^5 molecule cm^{-3} ,
201 and during flight B548 were 1.2×10^6 and 5.9×10^5 molecule cm^{-3} (Commane et al., 2010;
202 Stone et al., 2011; Stone et al., 2013).

203 Nitric acid and ammonia were measured using a CIMS (Chemical Ionisation Mass Spectrometry)
204 (University of Manchester); in this method the molecules are charged (soft ionization to form little
205 ion fragmentation) and then detected by a mass spectrometer (Le Breton et al., 2012; Von Bobruzki
206 et al., 2010).

207

208

209 **3. Observations**

210 The flight of the RONOCO campaign (B548) selected for this analysis has been chosen in order to
211 examine the London urban plume. The flight followed the route of the M25, a very busy and
212 congested 188 km long motorway that circumnavigates Greater London. The B548 flight was a
213 diurnal flight, carried out on 3 September 2010; the take-off occurred at 09:55 UTC, and after

214 running along the east coast of the UK made three anticlockwise M25 circuits at about 660 m of
215 altitude during which two missed approaches were made at Northolt (at about 11:35 UTC) and
216 Southend airports (at about 11:55 UTC). The landing occurred at 14:10 UTC. Fig. 1 shows the
217 flight track with the altitude. Analyzing the land use (figure not reported here) in the London urban
218 -suburban region and Reading, it is expected that the chemical processes that are relevant to the
219 troposphere in those regions are those typical of the urban and industrial environments.

220 The meteorological conditions which occurred during the flight can be derived analysing the 500
221 hPa geopotential height and the isobars field (NCEP reanalyzed data by www.wetterzentrale.de)
222 and the soundings observations (data available at <http://weather.uwyo.edu/upperair/sounding.html> -
223 Department of Atmospheric Science – University of Wyoming, USA), figures not showed here. The
224 B548 flight was characterized by a high pressure system over the UK: a wind field from North-East
225 is established over the central UK and London with weak intensity of about 5 knots and blue sky
226 (confirmed by the Nottingham balloon soundings (figure not reported here)).

227

228 **4. Data analysis**

229 **4.1 Data overview**

230 Fig. 2 shows the time series of NO_x (NO_2 measured by the TD-LIF instrument and NO by the
231 chemiluminescent), ΣANs (measured by TD-LIF), CO (measured by Aero Laser), O_3 (measured by
232 TECO), O_x ($O_3 + NO_2$) and altitudes.

233 Three large plumes of NO_x and CO , observed flying at constant altitude and well below the
234 boundary layer, are easily identifiable (Fig. 2). The PBL height was checked during the flight doing
235 a profile with the aircraft before starting the three runs around London: the meteorological and
236 chemical measurements confirmed the PBL level. During the flight, the wind blew in an easterly
237 direction from the North Sea inland (see Fig. 3), so that the west London region was downwind
238 from London so it is likely to have experienced transport of pollutants from London during the
239 morning rush hour. Moreover, the peak of the three plumes was measured each time the aircraft

240 flew over Reading (at constant altitude), a city in the county of Berkshire, where the NO_x reached
241 the maximum concentrations of about 30 ppb. Fig. 3 shows the NO_2 detected by the aircraft around
242 London area (upper panel) relative to each run along the M25: it is evident that during the flight
243 NO_2 concentrations are higher in the West London region (especially above Reading). In the bottom
244 panel of Fig. 3 the wind direction measured during the flight (black arrows) and the NO_2
245 concentration measured in three ground stations (H: Haringey, L: London and R: Reading) are
246 shown for each M25 run; it is possible to deduce that the NO_2 measured on the ground and that
247 measured in flight show similar features, with lower concentrations at Haringey and higher at
248 Reading.

249 As a result of the NO_x plumes a significant ozone titration phenomenon is found, with a strong O_3
250 reduction ($\Delta O_3 = -16$ ppb) reaching ~ 20 ppb (Fig. 2), the lowest value observed during the whole
251 flight. During the O_3 titration, a substantial increase of the ΣANs concentration was observed: the
252 increase measured was of about $\Delta \Sigma ANs = 3$ ppb (maximum value of ~ 3.5 ppb), probably due to the
253 local emissions of NO_x (Reading) and those transported from London. The high NO_x concentrations
254 above Reading, observed here, are in agreement with what observed by McMeeking et al. (2012), in
255 their flight above the M25 in June 2009. They measured similar concentrations of NO_x (about 30
256 ppb) and a ratio between O_3 and NO_x that decreases until the lowest concentration (around zero)
257 indicating a significant ozone titration processes in the London plumes, as found in our analysis.
258 Besides the analogously observed above Reading the flight studied in this work present similar
259 conditions of the flight of June 2009 reported by McMeeking et al. (2012) also in respect of the
260 highest concentrations measured in the West London region and wind flowing easterly. Here the
261 simultaneous measurements of compounds not observed in McMeeking et al. (2012), like ΣPNs ,
262 ΣANs and HNO_3 can help a further understanding of the chemistry around London focusing on the
263 O_3 budget (see below, section 4.3).

264

265 **4.2 Photochemical age: flight B548**

266 In this work we estimated the photochemical age of the air for the daytime diurnal flight B548 using
 267 both qualitative and quantitative methods. The ratio between NO_x and HNO_3 can be used as an
 268 approximate indication of the photochemical process state: it is expected that the ratio would
 269 decrease with increasing plume age (Perring et al., 2010). From the time series of the NO_x/HNO_3
 270 ratio (figure not reported here) two areas can be identified: East and West London regions,
 271 corresponding to those described in the paragraph 4.1. The qualitative photochemical process state
 272 estimation suggests that West London is impacted by relatively young air masses emitted locally.
 273 NO_x is emitted mainly as NO that reacts with ozone to form NO_2 , reaching equilibrium rapidly;
 274 during the daytime NO_x can be oxidized by OH , producing HNO_3 , or can react with RO_2 producing
 275 ΣPNs and ΣANs . The NO_y , therefore, is an indicator of the NO_x oxidation. Consequently, the ratio
 276 between NO_x and NO_y allows discrimination between fresh air and more aged air that is
 277 representative of more regional air mass (the NO_x/NO_y ratio decreases, with increasing NO_x
 278 oxidation).

279 Using the NO_x/NO_y ratio it is possible also to quantitatively estimate the photochemical age Δt
 280 that can be defined as (Kleinman et al., 2008; Slowik et al., 2011):

$$\begin{aligned} \frac{dNO_x}{dt} &= k_{NO_x+OH} [NO_x] [OH] \\ \int \frac{dNO_x}{NO_x} &= \int k_{NO_x+OH} [OH] dt \\ \frac{[NO_x]_t}{[NO_x]_0} &= \exp(-k_{NO_x+OH} [OH] \Delta t) \end{aligned} \quad (1)$$

281

282 To evaluate NO_x at time zero, we assume that all NO_y originates as NO_x ($[NO_x]_0 = [NO_y]$)

283 (Kleinman et al., 2008; Slowik et al., 2011) and equation (1) can be written as:

$$\Delta t = -\ln\left(\frac{[NO_x]_t}{[NO_y]_t}\right) \frac{1}{k_{NO_x+OH}[OH]} \quad (2)$$

284

285 For this analysis we used the mean *OH* concentration measured by the FAGE instrument during the
 286 M25 circuits, giving $[OH]=1.77\times 10^6$ molecules cm^{-3} . In Fig. 4 the values of the term
 287 $-\ln([NO_x]_t/[NO_y]_t)$ (at the top) and the photochemical ages (at the bottom) of the air masses
 288 sampled during the B548 flight are shown. The $-\ln([NO_x]_t/[NO_y]_t)$ term increases as the air
 289 masses become older and confirms the presence of two regimes (East and West London). As
 290 expected, the photochemical age is lower (ranging between 2 and 10 hr and a mean value of about 5
 291 hr) over the West London region that is a downwind of London area and over Reading (see Fig. 3)
 292 indicating that a fresh air plume originated in the London metropolitan area during the rush hour
 293 was advected to the west possibly taking in fresh emissions from urban areas on route (i.e. Reading
 294 town emissions).

295 In Fig. 5 (upper panel) the trends of the concentrations of NO_x , ΣPNs , ΣANs and HNO_3 measured
 296 along the M25 motorway as a function of the photochemical age calculated using equation (2) are
 297 shown. As expected, increasing the age of the plume decreases the NO_x level in favour of an
 298 increase of its oxidation products. Fig. 5 (lower panel) shows the dependence of the NO_y speciation
 299 on the photochemical age: the HNO_3 contribution to the NO_y increases in aged plumes and
 300 represents the principal NO_x reservoir (the NO_x/NO_y decreases from 0.81 to 0.32 (from 3 to 19 hours
 301 of aging); the HNO_3/NO_y increases from 0.13 up to 0.33 and the $\Sigma ANs/HNO_3$ increases from 0.08 up
 302 to 0.26).

303 In several studies the photochemical age of air masses has been estimated using *VOCs* ratios
 304 (Kleinman et al., 2003; Liggiio et al., 2010). Briefly, the photochemical age was based on
 305 differential gas phase reaction rates of toluene and benzene with the *OH* radical. The concentration

306 of the toluene resulting from *OH* oxidation can be calculated as a function of time ($C_T(t)$) (Liggio
 307 et al., 2010):

308

$$C_T(t) = C_T(0) \exp(-k_T[OH]t) \quad (3)$$

309

310 where $C_T(0)$ represents the initial concentration of the toluene and k_T the kinetic rate constant
 311 between toluene and *OH*. Using an equation similar to equation 3 for benzene, it is possible to
 312 evaluate its concentration at time t ($C_B(t)$); the ratio between the estimated concentrations of
 313 benzene and toluene ($R_{T/B} = C_T(t)/C_B(t)$) can be used to calculate the photochemical age of air
 314 masses:

$$AGE = \frac{\ln\left(\frac{R_{T/B}(t)}{R_{T/B}(0)}\right)}{(k_B - k_T)[OH]} \quad (4)$$

315

316 In our analysis, we cannot use this method because we do not have an initial concentration of
 317 toluene ($C_T(0)$) and benzene ($C_B(0)$) in order to calculate the age; but we can generate, using the
 318 lagrangian Hysplit model (Draxler et al., 2003), the back trajectories starting from a point along the
 319 flight trajectory (point R - Reading in Fig. 1) and understanding where the air mass was 5 hours
 320 before it was sampled. The air masses reach the area with highest NO_x (point R in Fig. 1 - above
 321 Reading - West London) at 11:00 UTC having come from over the London area earlier (air masses
 322 coming from a point in the center of the M25 circle, which is the London metropolitan area, at
 323 07:00 UTC). At point R (Fig. 1) the concentration of the toluene measured during the B548 flight
 324 was about 390 ppt (similar to the other values of toluene measured in the high NO_x area); we did a
 325 qualitative test to estimate which concentration of toluene should have been in point in the center of
 326 the M25 circle in order to measure 390 ppt of toluene in the point R, that is Reading in Fig. 1 (after
 327 5 hours). We found that the estimated $C_T(0)$ is about 460 ppt; Langford et al. (2010), between 20th

328 and 30th October 2006, measured concentrations of toluene on the Telecom tower (London) in the
329 range of ~200 and ~1800 ppt, it is possible, therefore, to deduce that the estimated $C_T(0) \approx 460$ ppt
330 is a credible value above London. Consequently, the estimation of 5 hours for the age of the air
331 mass is reasonable. McMeeking et al. (2012) calculated the photochemical age of the air masses
332 around London using the ratio between benzene and toluene, commonly used for this analysis
333 because of the different lifetimes of those species. In the London plume (downwind region, West
334 London) they found low benzene/toluene ratios and elevated pollutant concentrations corresponding
335 to fresh emissions, in other regions they measured high benzene/toluene ratios suggesting more
336 aged regional pollution or aged plumes from non-London sources. During RONOCO (B548 flight)
337 the ratio between toluene and benzene increases in the East London region and decreases in the
338 London plume side confirming the distinction between West and East London regions. In Fig. 6, the
339 benzene to toluene ratio and the O_3/NO_x ratio are shown: in respect to the East London region the
340 increase in the ratio between the two volatile organic compounds indicates more aged regional air
341 masses and the increase in O_3/NO_x implies a major level of the ozone concentrations; in contrast in
342 the West London regions the decrease in benzene to toluene ratios, corresponding to fresh
343 emissions and younger air masses, is coupled to a decrease of the O_3/NO_x suggesting ozone titration
344 processes as expected and explained previously. The correlation coefficient R between the O_3/NO_x
345 and the toluene to benzene ratio is of about 0.76.

346

347 **4.3 Ozone budget**

348 As illustrated in the Introduction, the diurnal ozone production can be evaluated studying which
349 termination of the reactions cycle (R1)-(R7) is dominant between the reactions (R1)-(R2) (alkyl
350 nitrate production) and (R1) (R3)-(R7) (ozone production). In our case study it is interesting to
351 evaluate the ozone removal and production since the high concentrations of ΣANs measured suggest

352 that the HO_x-NO_x coupled reactions cycles leads to a marked production of ΣANs to the detriment of
353 the ozone production.

354 The most significant mechanism of alkyl nitrate production is the reaction between RO_2 and NO ; it
355 is expected, therefore, that the $VOCs$ and NO_x are well correlated with ΣANs when they are formed.
356 We evaluated the correlation between the ΣANs and the NO_x and between ΣANs and different
357 $VOCs$; in Fig.7 and Fig.8 we reported the results of the scatter plot between the ΣANs and NO_x and
358 the toluene, selected for example. We found positive slopes and high correlation coefficients
359 confirming, then, the significant process of alkyl nitrate production that characterized the urban and
360 suburban area around London.

361 This is particularly true in the downwind regions (West London) where there are high
362 concentrations of NO_x , locally produced (as above Reading) and transported (as suggested by the
363 measured wind and the back trajectories analysis), demonstrating a reduction of the ozone
364 production in favour of alkyl nitrate production.

365 Several studies investigated the ozone production (Cazorla et al., 2012; Farmer et al., 2011;
366 Kleinman et al., 2005; Perring et al., 2010; Rosen et al., 2004) using different approaches. In our
367 analysis we used the model adopted by Cazorla et al. (2012). In their study, Cazorla et al. (2012)
368 measured the ozone production using a MOPS instrument and compared their measurements with
369 the calculated production rate of ozone (via reactions between HO_2 and RO_2 and NO) and the
370 modelled production rate of ozone (from a box model with the RACM2 mechanism); they found
371 that the measured and calculated P_{O_3} had similar peaks with a temporal shift during the morning in
372 the calculated P_{O_3} compared with the ozone production measured; the modelled, in contrast, was
373 about half the measured production rate. In our analysis, we calculated the ozone net production as
374 the difference between the production and the removal of ozone, following Cazorla et al. (2012):

$$P(O_3) = p(O_3) - l(O_3) \quad (6)$$

375

376 The production and removal ozone terms can be defined using the following kinetic equations:

$$p(O_3) = k_{HO_2+NO} [HO_2][NO] + \sum k_{RO_{2i}+NO} [RO_{2i}][NO] - P(\sum ANs) \quad (7)$$

$$l(O_3) = k_{OH+NO_2+M} [OH][NO_2][M] + k_{HO_2+O_3} [HO_2][O_3] \quad (8)$$

377

378 where $k_{HO_2+NO} = 3.3 \times 10^{-12} \exp(270/T)$, $k_{RO_{2i}+NO} = 2.6 \times 10^{-12} \exp(365/T)$, k_{OH+NO_2+M} has been

379 calculated as suggested in Sander et al. (2011), $k_{HO_2+O_3} = 1.0 \times 10^{-14} \exp(-490/T)$ (Sander et al.,

380 2011) and the $P(\sum ANs)$ term represents the alkyl nitrate production (see below). In order to

381 calculate the production of ozone (7), since RO_{2i} was not measured during the campaign, following

382 the assumption of Perring et al. (2010), we assumed that $[RO_{2i}] \sim [HO_2]$ and that a generic RO_2

383 behaves as $C_2H_5O_2$, and thus the rate $k_{RO_{2i}+NO}$ was chosen accordingly (Bardwell et al., 2005).

384 The alkyl nitrate production has been evaluated as (Farmer et al., 2011; Perring et al., 2010; Rosen

385 et al., 2004):

$$P(\sum ANs) = \sum_i \alpha_i k_{OH+RH_i} [OH][VOCs] \quad (9)$$

386 where α_i is the nitrate branching ratio defined as $\alpha = k_{R2}/(k_{R2} + k_{R3})$ (Perring et al., 2010; Rosen et

387 al., 2004) where k_{R2} and k_{R3} are the reaction constants of the reactions (R2) and (R3) (production of

388 alkyl nitrate and of O_3 (via NO_2 production)), respectively. The mean OH concentration measured

389 by the FAGE during the M25 circuits (1.77×10^6 molecule cm^{-3}) was used in the calculation, which

390 was the approach taken for the photochemical air mass evaluation. In Table 1 we summarized the

391 branching ratios α_i , the OH rate constants and the $VOCs$ concentrations used for the calculation of

392 the $\sum ANs$ production (9) and measured by the WAS-GC-FID instrument.

393 Calculating the ozone removal and production, we observed that the removal term $l(O_3)$ is on

394 average greater than the production term; in Fig. 9 (lower panel) is showed the ozone net production

395 during the diurnal flight B548: it is evident that the net production found is negative and that the

396 removal process is marked in the high NO_x region (solid circles - West London area with younger
397 air masses).

398

399 **Table 1.** The nitrate branching ratios α_i , the OH rate constants and the VOCs concentrations used
400 for the calculation of the ΣANs production (9) and measured by the WAS-GC-FID instrument.

401 Species reported in *Italic* are not measured during the campaign and estimate from previous

402 campaigns, see notes below.

VOCs	α_i	$\overline{\alpha_i}$	$k_{OH+VOCs}$ ($cm^3 molecule^{-1} s^{-1}$)	Concentrations (ppt)
Alkenes				
Ethene	0.0005	0.0086 ^a	8.20×10^{-12}	735
Propene	0.021		2.63×10^{-11}	150
1-Butene	0.039		3.14×10^{-11}	41
Trans-2-butene	0.041		6.40×10^{-11}	5
Isoprene	0.07	0.15 ^a	1.01×10^{-10}	66
Butadiene	0.04	0.11 ^a	6.66×10^{-11}	25
<i>Methylpropene</i>	<i>0.012</i>		5.14×10^{-11}	<i>200^b</i>
<i>2-methyl-1-butene</i>	<i>0.02</i>		6.07×10^{-11}	<i>100^b</i>
<i>3-methyl-1-butene</i>	<i>0.056</i>		3.18×10^{-11}	<i>30^b</i>
<i>2-methyl-2-butene</i>	<i>0.034</i>		8.69×10^{-11}	<i>130^b</i>
<i>c2-butene</i>	<i>0.041</i>		5.64×10^{-11}	<i>50^b</i>
<i>t2-pentene</i>	<i>0.064</i>		6.70×10^{-11}	<i>130^b</i>
<i>c2-pentene</i>	<i>0.064</i>		6.50×10^{-11}	<i>60^b</i>
Aromatics				
Benzene	0.029	0.10 ^a	1.22×10^{-12}	638
Toluene	0.079	0.10 ^a	5.96×10^{-12}	390
O-xylene	0.081	0.10 ^a	1.36×10^{-11}	110
M-P-Xylene	0.08	0.10 ^a	1.75×10^{-11}	281
Ethylbenzene	0.072	0.10 ^a	7.00×10^{-12}	96
<i>Propylbenzene</i>	<i>0.093</i>		5.80×10^{-12}	<i>40^c</i>
<i>3-Ethyltoluene</i>	<i>0.094</i>		1.86×10^{-11}	<i>90^c</i>
<i>4-Ethyltoluene</i>	<i>0.137</i>		1.18×10^{-11}	<i>30^c</i>
<i>1,3,5-Trimethylbenzene</i>	<i>0.127</i>		5.76×10^{-11}	<i>5^c</i>
<i>1,2,4-Trimethylbenzene</i>	<i>0.105</i>		3.25×10^{-11}	<i>90^c</i>
Alkanes				

Ethane	0.009	0.019 ^a	2.58×10^{-13}	3960
Propane	0.036		1.10×10^{-12}	1308
n-Butane	0.083		2.54×10^{-12}	1181
i-Butane	0.027	0.255 ^a	2.19×10^{-12}	640
i-Pentane	0.075	0.35 ^a	3.90×10^{-12}	530
2-3 Methylpentane	0.110	0.14 ^a	5.35×10^{-12}	230
Pentane	0.123		4.00×10^{-12}	250
Hexane	0.212		5.45×10^{-12}	87
Heptane	0.278		7.02×10^{-12}	56
Octane	0.346		8.71×10^{-12}	19
<i>Cyclopentane</i>	<i>0.10</i>		4.82×10^{-12} ^d	<i>190</i> ^b
<i>Cyclohexane</i>	<i>0.17</i>		6.96×10^{-12} ^d	<i>600</i> ^b
<i>Methylcyclohexane</i>	<i>0.17</i>		9.43×10^{-12} ^d	<i>300</i> ^b
<i>Nonane</i>	<i>0.393</i>		9.99×10^{-12} ^d	<i>50</i> ^b
<i>Decane</i>	<i>0.417</i>		1.12×10^{-11} ^d	<i>55</i> ^b
Other				
Acetylene	0.04		1.1×10^{-12}	450

403

404 Notes.

405 ^a The higher branching ratios used to calculate the alkyl nitrates production and taken from Rosen et
 406 al. (2004)

407 ^b Species not measured during the campaign and estimate from the measurements done by Perring
 408 et al. (2010)

409 ^c Species not measured during the campaign and estimate from the measurements done by Rosen et
 410 a. (2004)

411 ^d Rate constants by Gennaco et al. (2012)

412

413

414 The ratio between the ozone production (7) and the alkyl nitrates production (9) ($P_{O_3}/P_{\Sigma ANs}$) gives
 415 information about the balance of the two possible terminations of the reaction system (R1)-(R7);
 416 flying above the M25 motorway we calculated the $P_{O_3}/P_{\Sigma ANs}$. The $P_{\Sigma ANs}$ term was calculated using
 417 the branching ratios α_i and the concentrations of the VOCs measured (see Table 1) in flight and we

418 found that the ratio $P_{O_3}/P_{\Sigma ANs}$ varies between 20 and 2. In detail, calculating the ratio in the London
419 plume we estimated that $P_{O_3}/P_{\Sigma ANs} = 7$ (where the ozone production is 0.0385 ppt/s and the alkyl
420 nitrates production is 0.0054 ppt/s). Calculating the contribution to the $P_{\Sigma ANs}$ of each class of *VOCs*,
421 we found that they contribute almost for the same amount (36% Alkenes, 32% Alkanes, 31
422 Aromatics and 1% Acetylene). Moreover, the ratio between the ozone and the ΣANs production can
423 be evaluated directly using the measured concentrations of these species as the correlation slope
424 between the O_x (to take into account the ozone titration by *NO*) and the alkyl nitrates (Fig. 10). As
425 illustrated above, analyzing the ratio of O_x and ΣANs it is possible to determine which is the
426 dominant process between the production of O_x and the production of ΣANs . In Fig. 10 the
427 dependence between O_x and ΣANs during the M25 circuits of the B548 flight is shown; also in this
428 analysis it is possible identify two regimes: one for East, and another for West London. The
429 negative slope (grey circles) corresponds to older and cleaner air (probably emitted before sunrise
430 comparing its negative slope) with wind flowing from the North Sea (see Fig. 3); the positive one
431 (black circles) corresponds to high NO_x and younger air in the downwind of London region (see
432 Fig. 3). At least for these observations, the O_x vs ΣANs plot shows a slope of about 1 for the fresh,
433 urban plumes air (lower than 7 hours older). This slope is the lowest compared to that observed in
434 other megacities so far, as reported in Table 2, where the $P_{O_3}/P_{\Sigma ANs}$ at different sites is listed, as
435 well. In order to explain the London plume discrepancy between the value found for the calculated
436 $P_{O_3}/P_{\Sigma ANs}$ (about 7) and the measured $O_x/\Sigma ANs$ (about 1), we evaluated the alkyl nitrates production
437 increasing the branching ratios of some *VOCs* from the average to the maximum value of α_i ,
438 according with the analysis of Rosen et al. (2004) and Perring et al. (2010). The values are listed in
439 Table 1 and indicated as $\overline{\alpha_i}$. In this case we found that the $P_{O_3}/P_{\Sigma ANs}$ decreases to 4, suggesting that
440 a possible underestimation of the branching ratio for these species can explain at least part of the
441 disagreement between the calculated $P_{O_3}/P_{\Sigma ANs}$ and the observed $O_x/\Sigma ANs$. To take into account also

442 the contribution of some VOCs that we did not measure during the flight, we estimated the
 443 $P_{\Sigma ANs}$ assuming for these VOCs the concentrations collected by Rosen et al. (2004) and Perring et al.
 444 (2010) (these species are highlighted in Latin in the Table 1). This final simulation allows to reach a
 445
 446 **Table 2.** The $O_x/\Sigma ANs$ and $P_{O_3}/P_{\Sigma ANs}$ ratios in different sites.

Site	$O_x/\Sigma ANs$	$P_{O_3}/P_{\Sigma ANs}$	References
University of California-Blodgett Forest Research Station (UC-BFRS 2000-2001)	80	-	<i>Day et al., 2003</i>
Texas Air Quality Study (TexAQS-2000) Houston	29 (9-12 LT) – 41 (14-18 LT)	-	<i>Rosen et al., 2004</i>
Intercontinental Transport Experiment – Phase B (INTEX-B 2006) – Mexico city	17 (0-10 hr) – 90 (50 hr)	60 (0-10 hr)	<i>Perring et a., 2010</i>
Deepwater Horizon oil spill (2010) Gulf of Mexico	6.2 ÷ 7.9	8	<i>Neuman et al., 2012</i>
RONOCO (2010) London	~1	~7	<i>this study</i>

447
 448 value of $P_{O_3}/P_{\Sigma ANs}$ of 2 (where the ozone production is 0.0385 ppt/s and the alkyl nitrates production
 449 is 0.0162 ppt/s), which is significantly closer to the ratio between the productions obtained by the
 450 direct measurements of the ozone and alkyl nitrates concentrations. Also in this case we evaluated
 451 the role played by each VOCs to the production of alkyl nitrates: despite the contribution of the
 452 Alkenes remain almost unvaried (35%), the Aromatics become less important (23%) in behalf of
 453 the Alkanes (42%). This analysis suggests that the VOCs oxidation of the species measured and the
 454 average values of α_i (Perring et al., 2010) are not sufficient to justify the $P_{O_3}/P_{\Sigma ANs} = 7$ versus
 455 $O_x/\Sigma ANs = 1$. This may be because we are not taking into account unmeasured VOCs that may

456 contribute to the alkyl nitrate production. In consequence, the term of the ΣANs production is
457 underestimated and, therefore, the $P_{O_3}/P_{\Sigma ANs}$ overestimated. Using different and higher branching
458 ratios for the alkyl nitrates ($\overline{\alpha_i}$) and including unmeasured *VOCs* allowed to estimate better the
459 $P_{\Sigma ANs}$ and to reduce the discrepancy between measurements and calculations. In the Houston plume,
460 Rosen et al. (2004) found that $P_{O_3}/P_{\Sigma ANs} = 45$, the difference between this value and the ratio found
461 in the London plume is explained considering that the ozone production in Houston is about 50
462 times higher respect to the P_{O_3} in London and, on the contrary, the alkyl nitrate in Houston is only
463 two times greater than the ΣANs production in the London plume. Moreover, analyzing the time
464 series of NO_x , O_3 and ΣANs in Houston (Rosen et al., 2004), it is possible to verify the different
465 scenarios existing between London and Houston. In London, in fact, we found that in
466 correspondence of the high NO_x level, the ozone decreases significantly and the alkyl nitrates
467 increases; in Houston, on the other hand, when the ozone and the alkyl nitrates increase the NO_x
468 decreases. This is another indication of the different balance in the HO_x-NO_x reactions cycles
469 between Houston and London, in the latter, during the observations flight reported here, the high
470 NO_x emissions and the significant *VOCs* oxidation processes forming ΣANs involve a decrease in
471 the ozone level.

472

473 5. Conclusions

474 In this paper we presented the results of a daytime flight (B548) along the M25 motorway around
475 London. These observations confirm previous aircraft measurements of the pollutants species (NO_x
476 and ozone) around London, in particular the presence of high NO_x concentrations above Reading
477 (West London) (McMeeking et al., 2012). With the help of species not observed previously over
478 London, like ΣANs , ΣPNs and HNO_3 , here we had a chance to a deeper investigation of the
479 chemistry in the London area and the high level of NO_x over Reading. In correspondence of those

480 plumes strong ozone titration processes and significant high ΣANs concentration are observed. The
481 ozone and alkyl nitrate production analysis confirms that in the urban and suburban London area the
482 alkyl nitrate production plays an important role affecting the ozone budget, at least during the day
483 of observations reported here. The $P_{O_3}/P_{\Sigma ANs} = 7$, found calculating the alkyl nitrate production
484 considering only the *VOCs* measured in the flight is significantly different respect to the observed
485 $O_3/\Sigma ANs = 1$ that suggests a further study of the role played by the *VOCs* oxidation in the London
486 plumes. From sensitivity tests, made increasing the branching ratios of some *VOCs* and taking into
487 account the contribution of some unmeasured *VOCs*, we found that the calculated ratio $P_{O_3}/P_{\Sigma ANs}$
488 becomes 2, approaching notably the measured. This analysis suggests that attention must be paid
489 on the branching ratio of *VOCs* and on the Alkanes that play an important role in the alkyl nitrate
490 production in London affecting the local ozone production.

491

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499

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Figures captions

Fig. 1. B548 flight paths. The colour bar identifies the altitude; the capital letters indicate two airports (Southend (S) and Northolt (N)), the city of London (L) and Reading (R). The black lines represent the UK coast.

Fig. 2. B548 flight time series (the time is expressed in seconds after midnight, sec. A.M.). The green line represents the altitude and the grey square identify the M25 London circuit.

Fig. 3. On top: NO_2 (the colorbars on the right sides indicated the concentrations levels in ppbv) measured on flight during the three M25 circuits at 11:00 UTC, 12:00 UTC and 13:00 UTC, respectively. Bottom: the wind direction along the flight trajectory (grey arrows) and the NO_2 concentrations (colorbars on the right sides indicate the level in ppbv) measured in three ground stations (R = Reading, H = Haringey and L = London).

Fig. 4. On top: the $-\ln([NO_x]_t/[NO_x]_0)$ term of the equation (2) in the West and East London regions. At the bottom: the photochemical ages (hr) in the West and East London regions.

Fig. 5. On top: trends of the concentration of NO_x , ΣPNs , ΣANs and HNO_3 measured along the M25 motorway as function of the photochemical age. At the bottom: the dependence of the NO_y speciation from the photochemical age.

Fig. 6. Benzene to toluene ratio and the O_3/NO_x during the B548 flight.

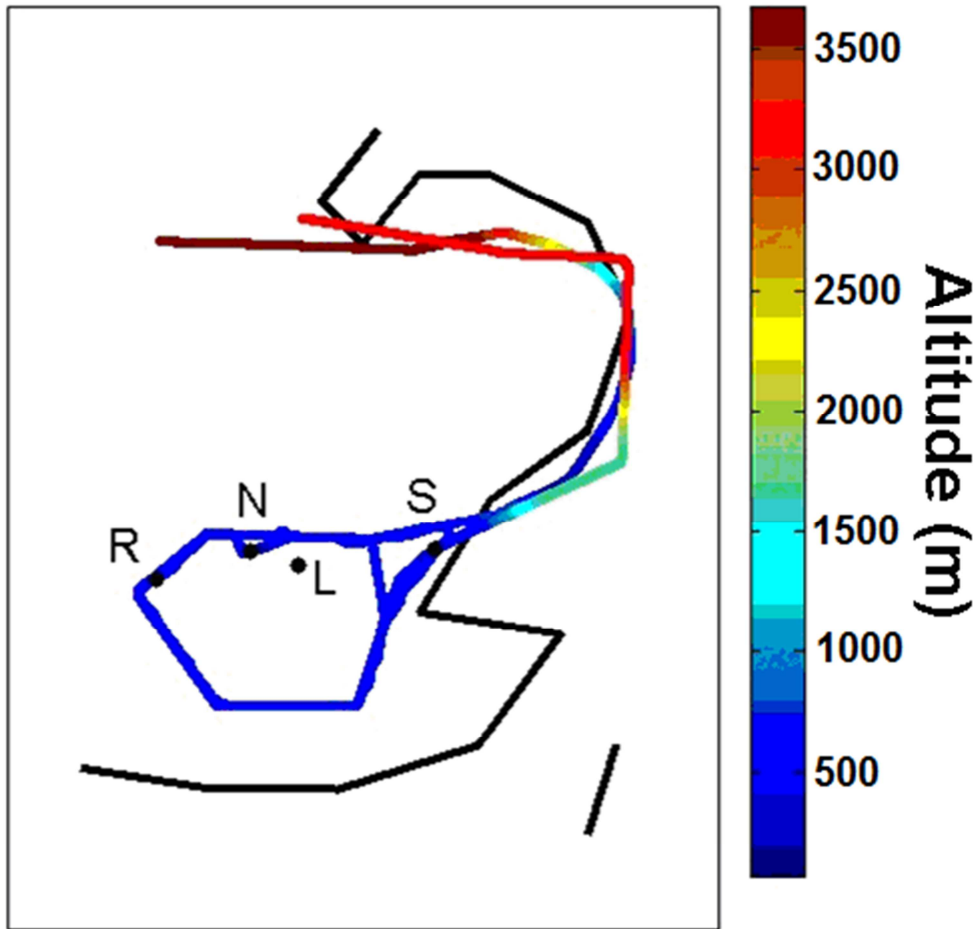
Fig. 7. Scatter plot between alkyl nitrates and NO_x . The grey points identify the East London plumes, the black points the London/Reading urban plumes. The linear fit and the correlation coefficients have been calculated for all the data.

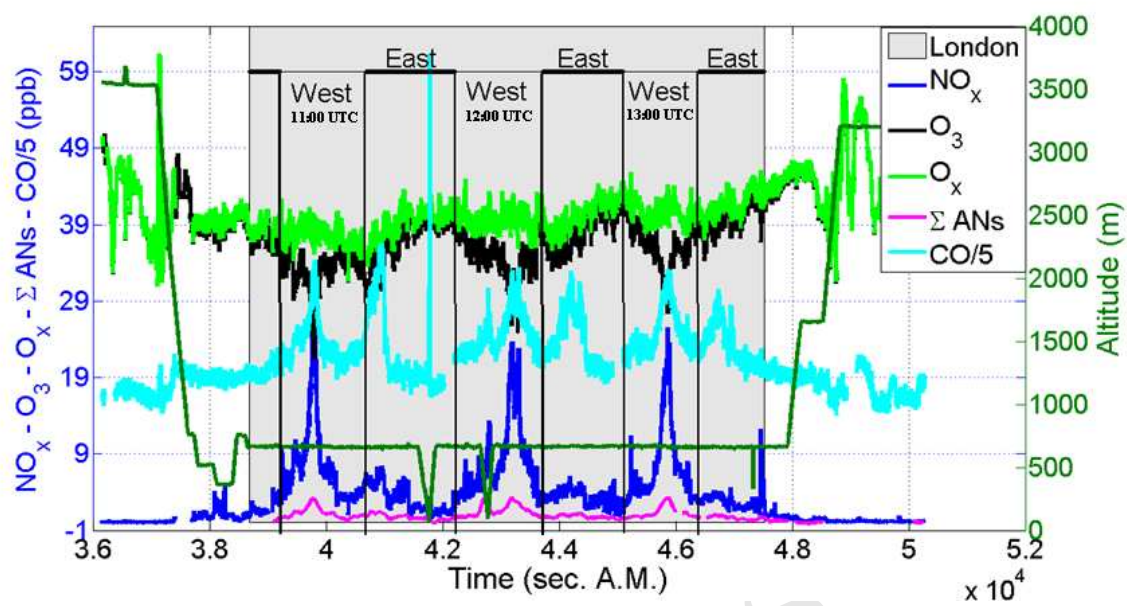
Fig. 8. Scatter plot between alkyl nitrates and toluene. The grey points identify the East London plumes, the black points the London/Reading urban plumes. The linear fit and the correlation coefficients have been calculated for all the data.

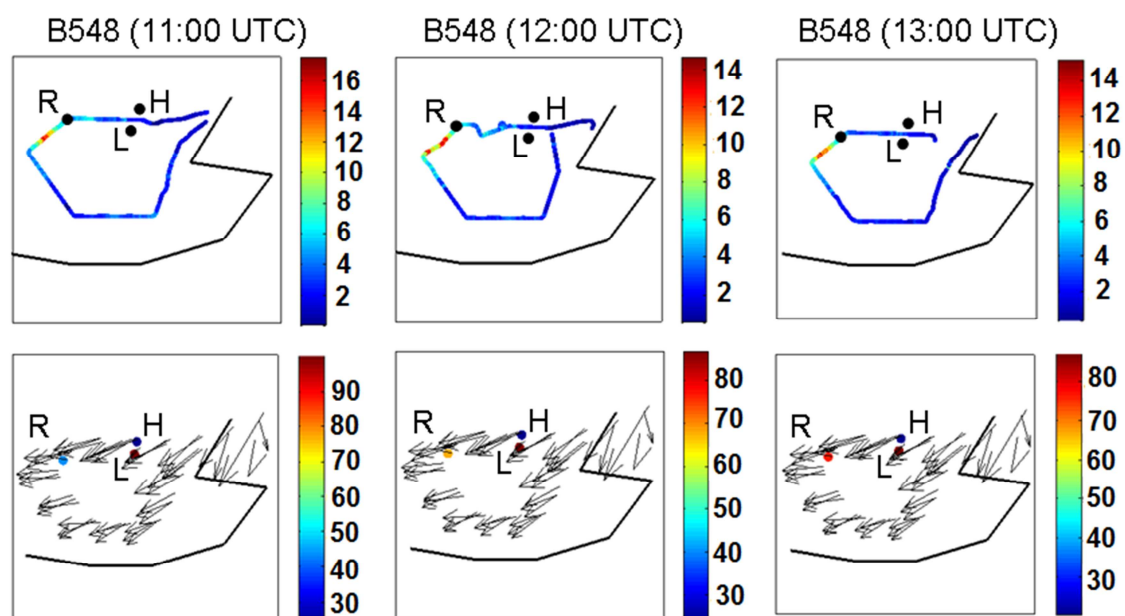
Fig. 9. At the top: the ozone production (black asterisk) and loss (black square) during the B548 diurnal flight calculated by equations (7) and (8), respectively. At the bottom: the net ozone production calculated for the diurnal flight B548: open circles identify the East London region (low NO_x , more aged air), solid circles identify the West London region (high NO_x , less aged air).

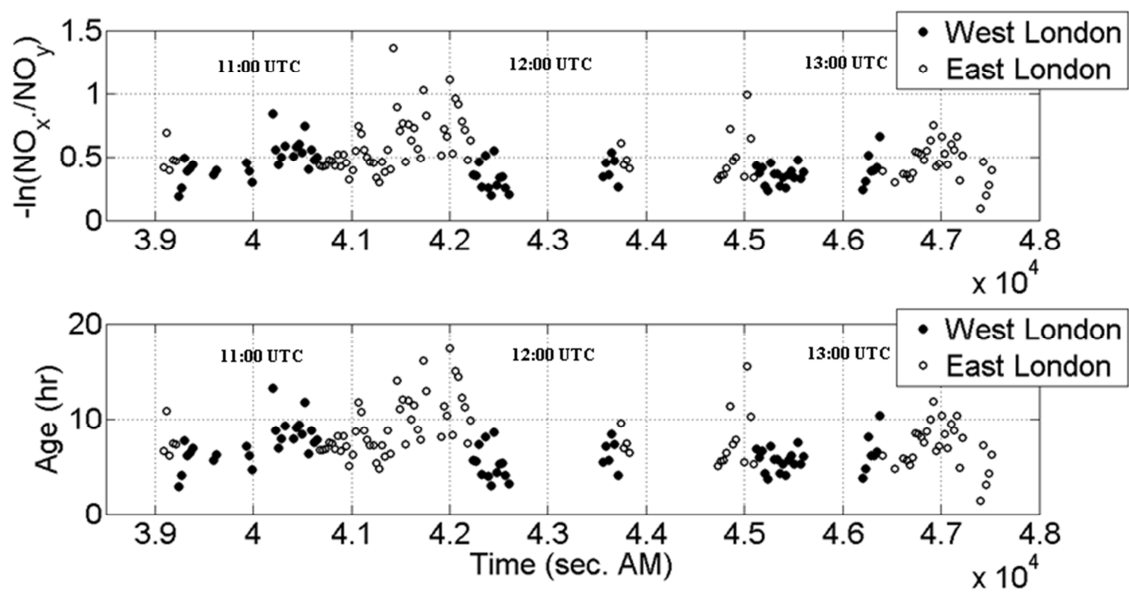
Fig. 10. The relation between O_x and ΣANs : we found two regimes (East London in grey points – West London in black points).

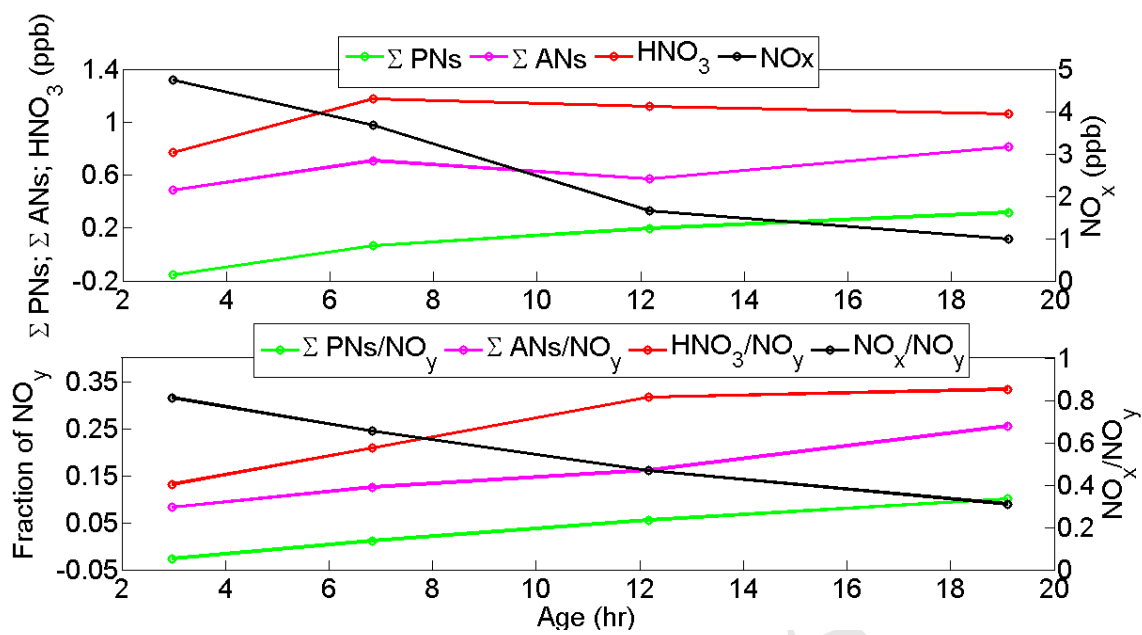
B548 (3/09/2010)

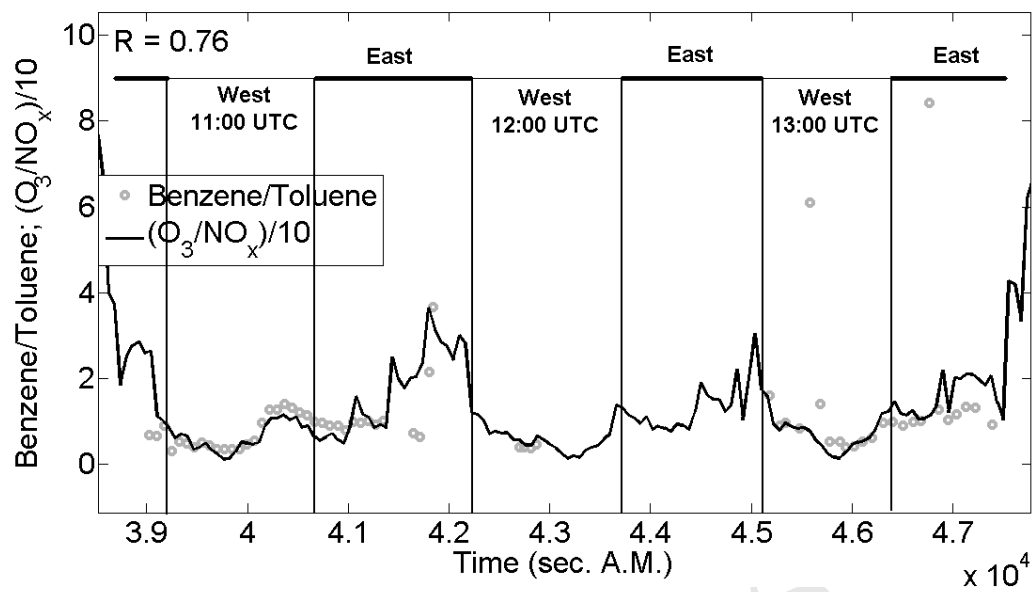


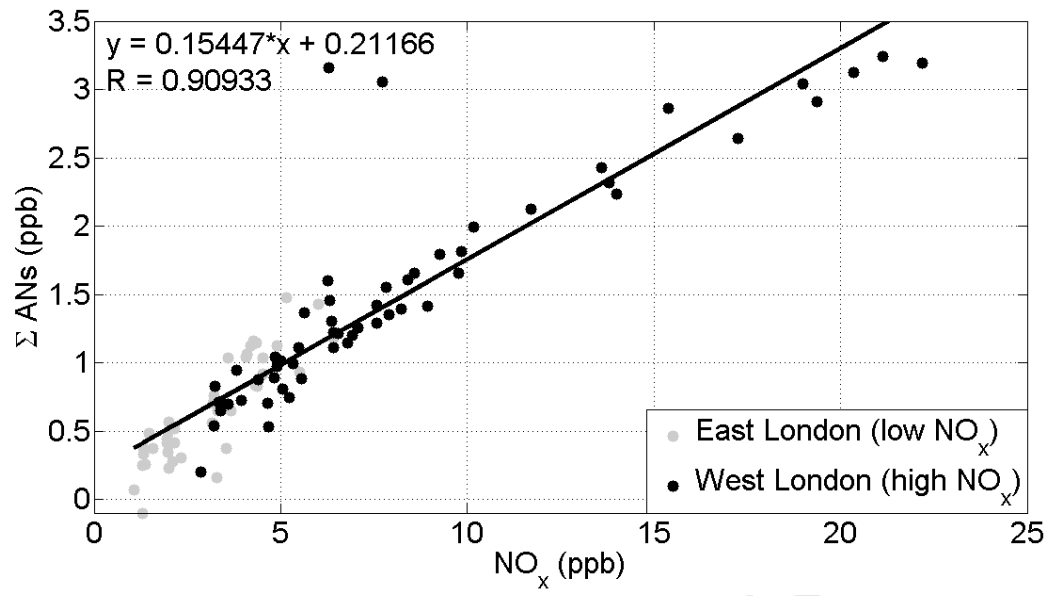


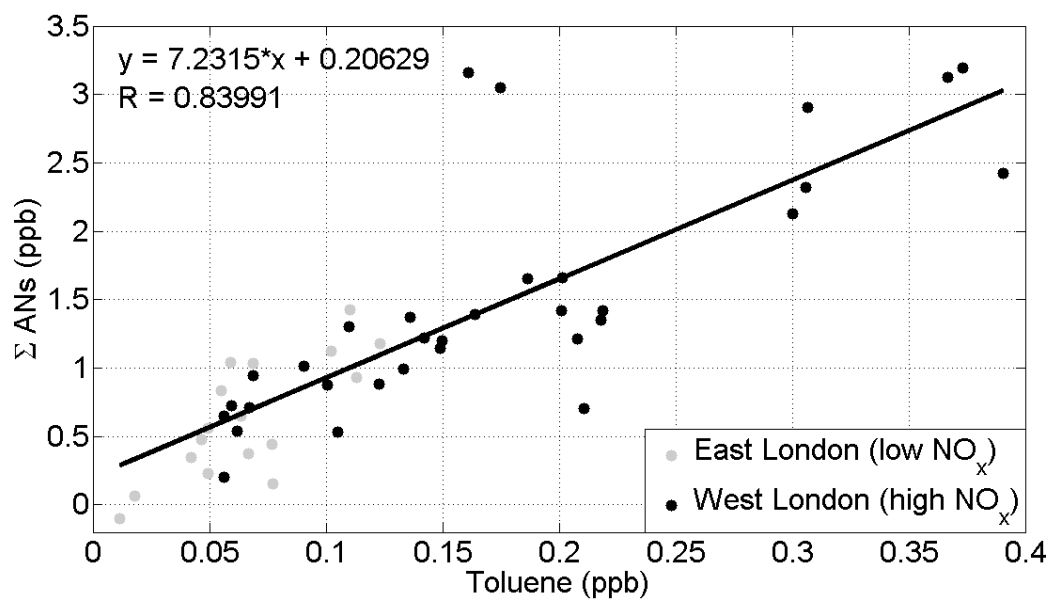


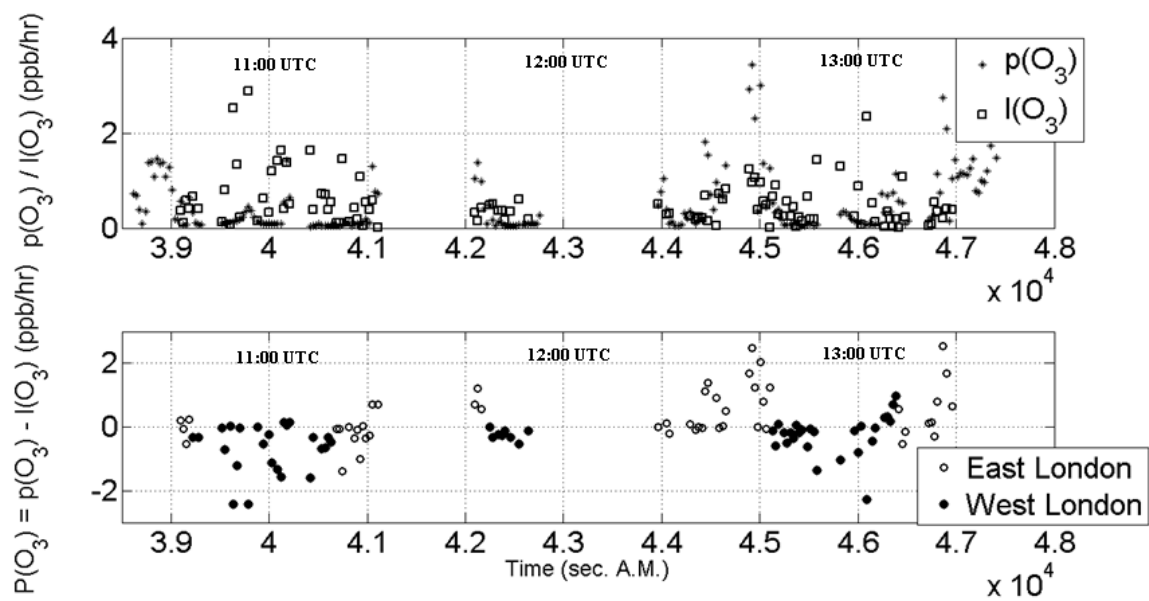


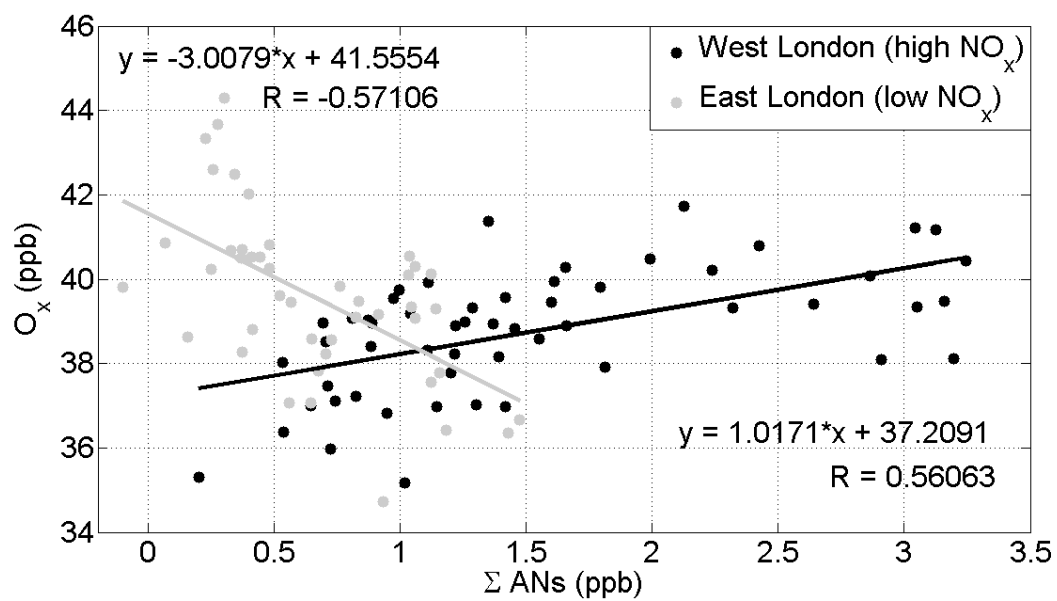












Highlights

- Daytime chemical and aerosol composition have been measured around London with an aircraft
- Unexpected high production of alkyl nitrate comparable to that of ozone
- The low O₃ production put the chemistry above London quite different compared with other megacities