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1 **Sources and atmospheric chemistry of oxy- and nitro-PAHs**
2 **in the ambient air of Grenoble (France)**

3
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28 **Abstract**

29 Total individual concentrations (in both gaseous and particulate phases) of 80 polycyclic
30 aromatic compounds (PACs) including 32 nitro-PAHs, 27 oxy-PAHs (polycyclic aromatic
31 hydrocarbons) and 21 parent PAHs have been investigated over a year in the ambient air of
32 Grenoble (France) together with an extended aerosol chemical characterization. The results
33 indicated that their concentrations were strongly affected by primary emissions in cold period,
34 especially from residential heating (i.e. biomass burning). Besides, secondary processes
35 occurred in summer but also in cold period under specific conditions such as during long thermal
36 inversion layer periods and severe PM pollution events. Different secondary processes were
37 involved during both PM pollution events observed in March-April and in December 2013. During
38 the first one, long range transport of air masses, nitrate chemistry and secondary nitro-PAH
39 formation seemed linked. During the second one, the accumulation of primary pollutants over
40 several consecutive days enhanced secondary chemical processes notably highlighted by the
41 dramatic increase of oxy-PAH concentrations. The study of the time trends of ratios of individual
42 nitro- or oxy-PAHs to parent PAHs, in combination with key primary or secondary aerosol species
43 and literature data, allowed the identification of potential molecular markers of PAH oxidation.
44 Finally, 6H-dibenzo[b,d]pyran-6-one, biphenyl-2,2'-dicarboxaldehyde and 3-nitrophenanthrene
45 have been selected to be the best candidates as markers of PAH oxidation processes in ambient
46 air.

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48 **Keywords:** PAH, OPAH, NPAH, Aerosol, SOA, reactivity

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58 **1. Introduction**

59

60 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental substances, mainly
61 emitted by anthropogenic incomplete combustion processes (Keyte et al., 2013; Ravindra et al.,
62 2008; Shen et al., 2013). PAHs are of major health concern, because of their carcinogenic,
63 mutagenic and teratogenic properties (IARC et al., 2010; Kim et al., 2013).

64 In the atmosphere, PAH oxidation through homogeneous and heterogeneous reactions lead
65 to the formation of oxy- and nitro-PAHs (Atkinson and Arey, 2007; Keyte et al., 2013). These
66 latter species are also emitted concomitantly with PAHs during incomplete combustion processes
67 (Chen et al., 2015; Karavalakis et al., 2010; Nalin et al., 2016). Oxy- and nitro-PAHs are
68 potentially more mutagenic than PAHs (Durant et al., 1996; Jariyasopit et al., 2014a, 2014b;
69 Pedersen et al., 2005; Rosenkranz and Mermelstein, 1985) and some of these substances are
70 also suspected to be carcinogenic (IARC 2012, 2013). The identification of the origins of oxy- and
71 nitro-PAHs is challenging, due to the coexistence of their primary and/or secondary sources
72 (Keyte et al., 2013). Several compounds have been identified as typical PAH oxidation by-
73 products and may be used as indicators of such chemical processes. For instance, (E)-2-
74 formylcinnamaldehyde and 6H-dibenzo[b,d]pyran-6-one are typical by-products of naphthalene
75 and phenanthrene oxidation processes, respectively (Lee et al., 2012; Sasaki et al., 1997).
76 Usually, molecular ratios between PAH derivatives and parent PAHs, or between well-known
77 secondary and primary compounds are calculated in order to highlight the influence of primary or
78 secondary oxy- and nitro-PAHs sources or to study the potential origin of these compounds. For
79 instance, the concentration ratio of 2-nitrofluoranthene (2-NFIt, a secondary compound, Arey et
80 al., 1986; Atkinson et al., 1990) to 1-nitropyrene (1-NP, a primary compound from diesel exhaust,
81 Keyte et al., 2016) has been extensively used to assess the primary vs secondary sources of
82 nitro-PAHs in ambient air (e.g. Albinet et al., 2007, 2008a; Bamford and Baker, 2003; Bandowe et
83 al., 2014; Cicciooli et al., 1996; Huang et al., 2014; Marino et al., 2000; Ringuet et al., 2012a, b;
84 Wang et al., 2014). Considering the same degradation rates for both compounds (Fan et al.,
85 1996), a ratio of [2-NFIt]/[1-NP] higher than 5 indicates the predominance of secondary formation

86 of nitro-PAHs while, a ratio lower than 5 highlights the strong influence of primary nitro-PAH
87 emission sources. Quinones-to-parent PAH concentration ratios have also been investigated in
88 order to evaluate the photochemical formation of oxy-PAHs during long range transport of air
89 masses (Alam et al., 2013, 2014; Harrison et al., 2016).

90 The overall objective of this work was to identify specific oxy- and nitro-PAHs, based on
91 ambient air field analysis combined with literature knowledge, that could further be used as
92 molecular markers of PAH oxidation and of secondary organic aerosol (SOA) formation in typical
93 urban environment. The individual annual concentration trends of these compounds, specifically
94 for substances known to be primary emitted or, conversely, by-products of secondary processes,
95 together with characteristic polycyclic aromatic compound (PAC: PAHs, nitro- and oxy-PAHs)
96 diagnostic ratios has also been investigated to evaluate the primary vs secondary sources of oxy-
97 and nitro-PAHs. This work is an additional analysis of the PAC data already reported in a
98 previous paper (Tomaz et al., 2016).

99

100 2. Experimental

101 2.1 Sampling site

102 The measurement site was located at the urban background sampling station of "Les
103 Frênes", (45° 09' 41" N, 5° 44' 07" E, 220 m above sea level) in Grenoble (France) (Fig. A1),
104 considered as the most densely populated urban area of the French Alps. The city is surrounded
105 by three mountainous areas. Earlier studies showed that residential heating, mainly biomass
106 combustion, accounts for the main source of PM_{2.5} during winter (Favez et al., 2010, 2012). In
107 addition to traffic and residential emissions, a cement and two power plants are also local PM
108 emitters. The frequent formation of thermal inversion layers in the Grenoble valley may lead to
109 the stagnation of pollutants enhancing the PM pollution events at ground level.

110 2.2 Sample collection

111 Samples have been collected every third day for one year from 01/02/2013 to 01/03/2014,
112 using two high volume samplers implemented in parallel (DA-80, Digital) (sampling duration 24 h,
113 30 m³ h⁻¹, PM₁₀ sampling head). The first high volume sampler was used to collect both gaseous
114 (polyurethane foams, PUF, Tisch Environmental, L = 75 mm) and particulate phases (PM₁₀,

115 Tissuquartz, Pallflex, $\varnothing = 150$ mm) for the quantification of PAHs, oxy- and nitro-PAHs. The
116 second sampler was only collecting particulate phase, in order to get a more comprehensive
117 chemical characterization (e.g. elemental carbon/organic carbon (EC/OC), anions, cations,
118 levoglucosan). Details on sample preparation and conservation have already been presented
119 (Tomaz et al., 2016) and are reported in the Supplementary Information A. A total of 123 samples
120 and 9 blanks were collected during this period and analyzed following the protocols described
121 below.

122 PM_{10} (TEOM-FDMS, TEOM 1405F, Thermo), NO_x (TEI 42I, Thermo) and O_3 (TEI 49I,
123 Thermo) concentrations were also monitored. Meteorological parameters (temperature, wind
124 direction, wind speed) were measured by the local air quality network in Grenoble (Air Rhône-
125 Alpes) and provided by ROMMA network (Meteorological network of the Alpine massif).
126 Temperature and pressure data from several locations at different altitudes were used to evaluate
127 the duration of thermal inversion layers in the Grenoble valley. Details are presented in the
128 Supplementary Information A.

129

130 2.3. Analytical procedures

131 Anions (Cl^- , NO_3^- , SO_4^{2-}), cations (NH_4^+ , Ca^{2+} , Na^+) and oxalate ($C_2O_4^{2-}$) were analyzed by
132 ion chromatography according to Jaffrezo et al. (2005). Levoglucosan was quantified using
133 HPLC-PAD (Waked et al., 2014) and EC /OC were measured using a Sunset lab analyzer using
134 the EUSAAR-2 thermal protocol (Cavalli et al., 2010).

135 PAHs, oxy-PAHs and nitro-PAHs were quantified using UPLC/UV-Fluorescence and
136 GC/NICI-MS, respectively, after PLE or QuEChERS-like extractions. Details of the analytical
137 procedures used have been previously reported (Albinet et al., 2006, 2014; Tomaz et al., 2016)
138 and are available in the Supplementary Information A (Tables A1, A2, A3 and A4).

139

140 2.4. Quality assurance and quality control

141 Accuracy of the analytical methods used in this work have been validated by the
142 participation to national and international inter-comparison exercises for the analysis of PAH,

143 EC/OC and levoglucosan. Results obtained were all in good agreement with reference values
144 (Panteliadis et al., 2015; Verlhac et al., 2013; Verlhac and Albinet, 2015).

145 PAH extraction efficiencies were evaluated following the EN 15549 and CEN/TS 16645
146 standard methods (CEN, 2008, 2014). Oxy- and nitro-PAH extraction efficiencies were quantified
147 using a certified solid material (urban dust, NIST SRM 1649b, Tables A5 to A7) and results were
148 in good agreement with NIST values and with those previously reported in the literature (Albinet
149 et al., 2014 and references therein). Additionally, an evaluation of the calibration drift and blank
150 contaminations was performed for data validation purposes. All collected data was corrected
151 using field blanks. Analytical method details are reported in the Supplementary Information A
152 (Tomaz et al., 2016).

153 Finally, the concentration values of OC, EC, anions, cations, oxalate, levoglucosan, 21
154 PAHs, 27 oxy-PAHs and 32 nitro-PAHs were validated and discussed in this work.

155

156 **3. Results and discussion**

157 *3.1. Overview of PM chemical composition and pollution events*

158 The year 2013 was affected by two severe national PM pollution events (PM_{10} concentrations
159 $> 50 \mu\text{g m}^{-3}$ for at least 3 consecutive days) occurring during the cold season (defined as the
160 period from January 1st to April 10th and from the October 1st to December 31st 2013). They were
161 observed on all the northern part of France from 02/25/2013 to 04/08/2013, and from 12/09/2013
162 to 12/19/2013 (Figs. 1, A31 and A32).

163

164 The first PM pollution event could be divided into two parts (Fig. 1):

165 - February-March (02/25/2013-03/05/2013) with $63 \mu\text{g m}^{-3}$ of PM_{10} concentration levels on
166 average and with a large contribution of OM to the total PM composition and the presence of a
167 thermal inversion layer.

168 - March-April (03/24/2013-04/08/2013) with PM_{10} concentration levels around $50 \mu\text{g m}^{-3}$ and
169 with a large contribution of secondary inorganic species (ammonium nitrate and sulfate) to the
170 total PM composition and the absence of thermal inversion layer.

171 Similarly to the first PM pollution event, a second event was observed in December, with
172 PM₁₀ concentrations about 56 µg m⁻³ on average and with a large contribution of organic matter
173 (OM) to the total PM composition and the occurrence of thermal inversion layers over a long
174 period (10 consecutive days).

175

176 3.2. Annual trends of individual compounds

177 The annual concentration trends of individual compounds were similar for all PAHs, oxy- and
178 nitro-PAHs, with higher concentrations observed in winter and autumn than in spring and summer
179 (Figs. 2, A6 to A26). Additional emission sources, namely residential heating, and the occurrence
180 of thermal inversion layers in the Grenoble valley leading to the accumulation of pollutants (Fig. 1)
181 explain the high concentrations observed in winter and autumn. Lower concentrations in summer
182 and spring are due to lower PAC emissions and their degradation by photochemical processes,
183 as already highlighted in a previous paper (Tomaz et al., 2016).

184 Overall, significant correlations (Pearson coefficient $R > 0.6$, $n = 123$, $p < 0.05$, Supplementary
185 Information B, Table B1) between known primary compounds such as EC, NO, levoglucosan,
186 PAHs and a large number of oxy- (18 compounds over 27 oxy-PAHs) and nitro-PAHs (12
187 compounds over 32 nitro-PAHs) were observed (total concentrations for PACs: gaseous +
188 particulate phases). However, these results should be discussed cautiously to avoid spurious
189 deductions from the statistical analysis. As an example, the concentrations of levoglucosan, a
190 specific marker of biomass burning (Simoneit et al., 1999), significantly correlated with those of 1-
191 nitropyrene ($R = 0.89$, $p < 0.05$, $n = 123$, Table B1), which is a well-known marker of diesel emissions
192 (Keyte et al., 2016). In addition, these correlations could also indicate that these compounds are
193 sorbed together or have similar fates. The local atmospheric dynamic of the valley with the
194 frequent formation of inversion layers is one of the key parameter leading to such correlations
195 (Fig. 1).

196 Only three substances, namely phthalaldehyde, biphenyl-2,2'-dicarboxaldehyde, and 1,2-
197 naphthoquinone, showed a distinct annual pattern with higher concentrations during spring and
198 summer than in winter and autumn (Figs. 2 and A12, A13, A14). These specific patterns seem to
199 be related to their formation by secondary photochemical processes:

- 200 - Phthalaldehyde is known as a second generation product of naphthalene
201 photooxidation (i.e. from the oxidation of (E)-2-formylcinnamaldehyde) (Bunce et al.,
202 1997; Chan et al., 2009; Kautzman et al., 2010; Lee and Lane, 2009; Wang et al., 2007a).
203 To the best of our knowledge, phthalaldehyde has been observed in the emissions of
204 primary combustion sources (wood burning) only at very low concentration levels (Nalin et
205 al., 2016). The non- correlation, on yearly basis ($R=0.2$, $n=123$, $p>0.05$), between (E)-2-
206 formylcinnamaldehyde and phthalaldehyde shows that the latter is also a secondary by-
207 product of other parent compounds and not only PAHs. For instance, phthalaldehyde
208 has been identified as an oxidation product from tolualdehyde photolysis (Clifford et al.,
209 2011).
- 210 - 1,2-Naphthoquinone has been identified in diesel and gasoline exhausts (Cho et al.,
211 2004; Jakober et al., 2007; Oda et al., 2001) but has also been reported as an OH-
212 initiated oxidation product of naphthalene (Lee and Lane, 2009).
- 213 - Biphenyl-2,2'-dicarboxaldehyde has been identified in primary emissions from biomass
214 burning at very low concentration levels (Nalin et al., 2016). It has been reported as a
215 secondary compound from the gas phase reaction of phenanthrene with OH radical (Lee
216 and Lane, 2010), NO_3 radical (Wang et al., 2007b), and O_3 (Kwok et al., 1994; Wang et
217 al., 2007b; Zhang et al., 2010). This compound has also been identified as a by-product
218 of the heterogeneous reaction of phenanthrene with ozone (Perraudin et al., 2007; Zhang
219 et al., 2010).

220

221 3.3. Formation of nitro-PAHs: study of the [(2+3)-NFlt]/[1-NP] ratio

222

223 The primary emissions vs the gas-phase formation of nitro-PAHs in ambient air was
224 assessed using the (2+3)-nitrofluoranthene-to-1-nitropyrene ($[(2+3)\text{-NFlt}]/[1\text{-NP}]$) concentration
225 ratio (total concentrations) (Fig. 3).

226 The annual mean value of the $[(2+3)\text{-NFlt}]/[1\text{-NP}]$ concentration ratio of 6.3 ± 3.9 indicates a
227 slight predominance of secondary formation of nitro-PAHs in the gas phase. The highest $[(2+3)\text{-}$
228 $\text{NFlt}]/[1\text{-NP}]$ values (>10) were surprisingly observed during the winter period and in early spring

229 (from January to April 2013) while previous studies reported high ratio values in summer and low
230 ones in winter (Albinet et al., 2007, 2008a, b; Bamford and Baker, 2003; Dimashki et al., 2000;
231 Ringuet et al., 2012a, b). Only a few studies reported similar results with ratios larger than 5 in
232 winter; that were explained by specific conditions such as pollutant accumulation over several
233 days (Albinet et al. 2008a; Lin et al. 2015).

234 Here, the two highest ratios were observed during the March-April period together with high
235 PM_{10} concentration levels. During this period, the [(2+3)-NFlt]/[1-NP] ratio was significantly
236 correlated with NO_3^- (Pearson coefficient: $R=0.75$, $p<0.05$, $n=6$), suggesting a link between the
237 secondary formation of nitro-PAHs and the nitrate chemistry. Conversely, at the end of the
238 February-March PM pollution event, a large NO_3^- contribution was observed but no significant
239 correlation between nitrate and the [(2+3)-NFlt]/[1-NP] ratio was noticed ($R=-0.3$, $p>0.05$, $n=4$)
240 (Fig. 3). The organic matter (OM) formed the main fraction of PM_{10} mass in this last period and
241 originated mainly from biomass burning (residential combustion), as indicated by the high
242 concentrations of levoglucosan. Under these conditions, nitrate was probably emitted by biomass
243 burning as supported by its correlation with levoglucosan ($R=0.85$, $p>0.05$, $n=4$). This result
244 shows the existence of a link between the secondary origin of nitrate and the sources of nitro-
245 PAHs in relation with photochemical conditions. High NO_3^- concentrations could be explained by
246 the oxidation of NO_2 , that may be also able to react with PAHs to form nitro-PAHs after initiation
247 by OH and/or NO_3 radicals.

248 In summer, several [(2+3)-NFlt]/[1-NP] ratios were higher than 5 for periods characterized by
249 high SO_4^{2-} contributions to PM_{10} , indicating the impact of atmospheric secondary processes with
250 an enhancement of the photochemical activity, possibly leading to the secondary formation of
251 nitro-PAHs.

252 253 3.4. Cold season: influence of primary emissions and evidence of secondary formation processes 254 under specific conditions

255 As discussed in the paragraph 3.3., the February-March period of the first PM pollution event
256 seemed mainly influenced by primary emissions. In fact, wind speeds were low during this period,

257 with an average value of 5 km h^{-1} , inducing a low atmospheric dispersion. As shown by the
258 results of the non-parametric wind regression analysis (NWR, Henry et al., 2009) performed using
259 Zefir tool (Petit et al., 2016), sources of PM_{10} seemed mainly local (Fig. 5). The low dispersion
260 together with the formation of thermal inversion layers (Fig. 1) enhanced the stagnation of the
261 pollution in the valley and the increase of primary pollutant concentrations. High concentrations of
262 many oxy- (14 oxy-PAHs) and nitro-PAHs (6 nitro-PAHs) were observed during this period. Some
263 substances showed their highest concentrations of the year at that time, such as 1-
264 naphthaldehyde, 1,4-naphthoquinone, 9-nitroanthracene, 2-nitroanthracene, 5-
265 nitroacenaphthene, and 7-nitrobenz[a]anthracene (Figs. 4, A12, A21, A22, A23, A24). All of them
266 may originate from both primary and secondary sources (Arey et al., 1989; Atkinson and Arey,
267 1994; Chen and Zhu, 2014; Chen et al., 2015; Huang et al., 2013; Karavalakis et al., 2010; Liu et
268 al., 2015; Sauret-Szczepanski and Lane, 2004). The potential occurrence of secondary formation
269 of nitro-PAHs is indeed highlighted by the high $[(2+3)\text{-NFlt}]/[1\text{-NP}]$ ratio observed, with a value of
270 11, when PM_{10} concentrations were the highest (on February 28) (Fig. 3). It is therefore likely that
271 both primary emissions and secondary processes were enhanced during this period.

272
273 In comparison with the first part of the PM pollution event, during the March-April period,
274 lower concentrations of primary compounds such as, NO , NO_2 , levoglucosan and 1-nitropyrene
275 were observed, together with a lower contribution of OM to the PM concentrations. Conversely,
276 concentrations of secondary species such as ammonium, nitrate and sulfate, (E)-2-
277 formylcinnamaldehyde (Aschmann et al., 2013; Kautzman et al., 2010) and, as shown before,
278 $[(2+3)\text{-NFlt}]/[1\text{-NP}]$ ratios (from 7 to 13), were significantly higher (Figs. 3 and 4). This period was
279 thus characterized by the transport of aged air masses, coming from the N-NE, to the sampling
280 site of Les-Frênes (Figs. A27 and A28) and the absence of thermal inversion layers in the
281 sampling area (Fig. 1). The secondary formation of nitro-PAHs, together with the nitrate
282 chemistry, and, to a lesser extent, of oxy-PAHs, may have occurred during the transport and
283 aging of these air masses.

284

285 The December pollution event was characterized by a dramatic increase of the
286 concentrations of all pollutants except ozone (Figs. 1, 2, 3, 4 and A4 to A19). Concentrations of
287 primary species such as EC ($7.80 \mu\text{g m}^{-3}$), some PAHs (11 PAHs, from 0.4 ng m^{-3} for 2-
288 methylfluoranthene to 48.6 ng m^{-3} for 2-methylnaphthalene), levoglucosan (2963 ng m^{-3}), 1-
289 nitropyrene (46 pg m^{-3}) and NO (about $110 \mu\text{g m}^{-3}$) showed their highest yearly concentrations,
290 highlighting the impact of local combustion sources like residential heating (notably wood
291 combustion) and traffic. Additionally, low wind speed ($< 10 \text{ km h}^{-1}$) and the occurrence of strong
292 and durable thermal inversion layers (from 18 to 24 h per day during the overall PM event)
293 promoted the accumulation of pollutants in the Grenoble valley (Figs. 1, 5 and A3).

294
295 The highest concentrations of several individual nitro- and most of the oxy-PAHs were
296 observed during this event (Figs. 4, A12 to A26). Total oxy-PAH concentrations ($\Sigma_{27}\text{oxyPAHs}$)
297 was even higher than total PAH concentrations ($\Sigma_{21}\text{PAHs}$) i.e. about 183 and 136 ng m^{-3} ,
298 respectively (Tomaz et al., 2016). Concentrations of many PAH derivatives were more than 10
299 times higher (ranging from 11 to 43) than the annual mean concentration levels, including phthalic
300 anhydride, (E)-2-formylcinnamaldehyde, 1-acenaphthenone, 1,2-naphthalic anhydride, xanthone,
301 acenaphthenequinone, 6H-dibenzo[b,d]pyran-6-one, 9,10-anthraquinone, 1,8-naphthalic
302 anhydride, 1,4-anthraquinone, 2-methylanthraquinone, 9-phenanthrenecarboxaldehyde, 2-nitro-9-
303 fluorenone, benzo[a]fluorenone, benzo[b]fluorenone, benzanthrone, 1-pyrenecarboxaldehyde,
304 aceanthrenequinone, benz[a]anthracene-7,12-dione, and 9-methyl-10-nitroanthracene. Low wind
305 speeds and any potential long range transport could not alone explain the dramatic increase of
306 their concentrations (Fig. 5). Parent PAHs were accumulated for several consecutive days due to
307 the low wind speeds and the long-time inversion layers formed (Figs. 1 and A3). In the presence
308 of atmospheric oxidants – such as OH radical, for which concentration levels are usually high in
309 urban environments even in winter (Heard et al., 2004) - the accumulation of PAHs allowed
310 enough time for their oxidation, the formation of by-products such as oxy-PAHs through gaseous
311 and/or heterogeneous processes and their accumulation. Interestingly, secondary processes
312 involved during the December PM pollution event seemed different than those involved during the

313 first observed in February-March. Actually, only oxy-PAHs and no nitro-PAHs were effectively
314 formed, as supported by the low [(2+3)-NFlt]/[1-NP] ratio value of 3.9.

315 As an example of evidences of secondary oxy-PAH processes during this period, (E)-2-
316 formylcinnamaldehyde concentrations were the highest during this PM pollution event (Fig. 6).
317 This compound originates from naphthalene oxidation (Nishino et al., 2012; Sasaki et al., 1997;
318 Wang et al., 2007a). No significant correlation with any primary compound was observed on the
319 annual scale (e.g. with levoglucosan and 1-nitropyrene; $R < 0.4$, excluding the December event,
320 $n=120$, $p < 0.05$) confirming the secondary origin of this compound. Interestingly, concentrations
321 of phthalaldehyde increased when its precursor concentration decreased and, were maximum
322 on the 12/16/2013. Here again, the secondary processing during the PM pollution event seemed
323 obvious and preponderant. Besides, phthalic anhydride, an oxidation product of phthalaldehyde
324 (Wang et al., 2006), was measured in large concentration (42 ng m^{-3}) with a maximum value
325 reached at the same time as (E)-2-formylcinnamaldehyde. Discrepancy of temporal concentration
326 trend was probably due to the dual origin of phthalic anhydride with also its direct emission by
327 combustion processes and especially diesel exhaust (Fig. 6) (Bayona et al., 1988; Sidhu et al.,
328 2005).

329

330 3.5. Warm season: Influence of photochemistry and identification of potential markers of PAH 331 oxidation processes

332 Using both gaseous and particulate phase concentrations, the ratios of oxy- or nitro-PAHs
333 to their parent PAH have been considered in order to investigate the PAH relative reactivity and
334 the sources of oxy- and nitro-PAHs. Note that acenaphthenequinone and acenaphthenone may
335 arise from the oxidation of both, acenaphthene and acenaphthylene but the latter one was not
336 quantified in our study so, the ratios were calculated using acenaphthene only (Zhou and
337 Wenger, 2013).

338 Overall, only concentration ratios to their parent PAHs of 6H-dibenzo[b,d]pyran-6-one, 3-
339 nitrophenanthrene, biphenyl-2,2'-dicarboxaldehyde, 9,10-anthraquinone, 2-methyl-4-
340 nitronaphthalene and 6-nitrobenzo[a]pyrene showed a trend with significant higher values
341 exclusively in the warm season (defined as the period from the 04/11/2013 to the 09/30/2013)

342 (Figs. 7, A33, A34 and A35). This suggests the dominant secondary origin of these specific
343 species. By comparison, known primary compounds such as 1-nitropyrene and
344 benz[a]anthracene-7,12-dione did not exhibit the same trend. Note that, peak values of the
345 concentration ratios in November were observed for all compounds and could be explained by
346 the very low concentration levels of both parent PAHs and PAH derivatives (inducing larger
347 uncertainties).

348
349 The highest concentration ratios of the selected secondary candidate compounds were
350 observed in July and August (Fig. 7, period framed). At the same time, [(2+3)-NFIt]/[1-NP] ratio
351 was higher than 5 (with an average of 9) suggesting favorable photochemical conditions to induce
352 a secondary formation of nitro-PAHs. Concentrations of oxalate, a marker of secondary
353 processes for the organic matter (Carlton et al., 2007; Legrand et al., 2007; Warneck, 2003), were
354 also high (and the highest of the year, from 350 to 401 ng m⁻³, Fig. 7) confirming the influence of
355 the photochemical activity during this period. The whole period was characterized by long range
356 transport, with air masses coming from the North or the South of the sampling location (e.g. Figs.
357 A29 and A30). Significant correlations between total concentrations of 6H-dibenzo[b,d]pyran-6-
358 one with 9,10-anthraquinone (R=0.93), 3-nitrophenanthrene (R=0.96) were obtained (from July to
359 August, n=21, p<0.05). Only biphenyl-2,2'-dicarboxaldehyde was not significantly correlated with
360 any identified secondary candidate compounds. Different chemical processes, unknown at the
361 moment, may be involved for this last compound.

362
363 All of these compounds have been previously reported in the literature as by-products of
364 gas phase and/or heterogeneous reactions of PAHs (Lee and Lane, 2009, 2010; Perraudin et al.,
365 2007; Reisen and Arey, 2002; Zhang et al., 2011; Zhang et al., 2013). However, except biphenyl-
366 2,2'-dicarboxaldehyde, they also have all been identified in primary emissions from biomass
367 burning or vehicle exhaust (Alves et al., 2016; Bayona et al., 1988; Fine et al., 2001; Fine et al.,
368 2002; Fitzpatrick et al., 2007; Nalin et al., 2016; Zielinska et al., 2004).

369 The question to be answered is to identify which compounds could be here considered as
370 a marker of oxidative processes involving PAHs to better understand the sources of these toxic

371 compounds. Ideal marker compounds should mainly be specific of secondary processes,
372 relatively stable in the atmosphere and easily quantified. 2-Methyl-4-nitronaphthalene and 6-
373 nitrobenzo[a]pyrene are rejected according to these criteria, as they are usually (like in this study)
374 observed at very low concentration levels in the atmosphere and quite difficult to quantify. 9,10-
375 Anthraquinone does not seem to be a good marker candidate of PAH oxidation processes as it
376 has been reported as largely emitted by vehicular emissions (Alves et al., 2016). Lee et al. (2012)
377 suggested the use of 6H-dibenzo[b,d]pyran-6-one as a SOA marker for phenanthrene
378 photooxidation. Here, in July-August 2013, low concentrations of this compound were observed
379 during the days significantly impacted by primary emission sources (with high EC concentrations,
380 Fig. 7). This indicates that it may mainly arise from secondary reactions and not from primary
381 emission sources. 3-Nitrophenanthrene has also been reported as a by-product of SOA formation
382 from phenanthrene oxidation (Di Filippo et al. 2010; Lin et al. 2015).

383

384 Finally, only 6H-dibenzo[b,d]pyran-6-one, biphenyl-2,2'-dicarboxaldehyde and 3-
385 nitrophenanthrene remain interesting candidates as markers of secondary reactions. 6H-
386 Dibenzo[b,d]pyran-6-one has also the advantage to be present in large concentrations in the
387 atmosphere by comparison to nitro-PAHs (about 2 orders of magnitude more abundant) allowing
388 an easier quantification.

389

390 4. Conclusion

391 Individual concentrations of about 60 oxy- and nitro-PAHs were measured over a year in
392 Grenoble-Les Frênes, jointly with specific primary or secondary aerosol species. In cold period,
393 oxy- and nitro-PAH concentrations were controlled by emissions from residential heating (e.g.
394 biomass burning) together with secondary processes occurring under specific conditions such as
395 pollutant accumulation or long range transport of air masses. The study of the time trends of the
396 ratios of oxy- or nitro-PAHs on parent PAH concentrations highlighted higher ratios of a series of
397 compounds in summer, concurrently with high oxalate concentrations. By combination with
398 literature data, 6H-dibenzo[b,d]pyran-6-one, biphenyl-2,2'-dicarboxaldehyde and 3-
399 nitrophenanthrene have been identified as probably good marker candidates of PAH oxidation

400 processes in ambient air.

401 The approach to identify specific PAH derivatives typical of PAH oxidation and SOA formation
402 based on ambient air field analysis combined with literature knowledge proposed here is limited
403 by the time resolution of the PAC measurements as well by the current knowledge available in
404 the literature. Further work will be needed to document the behavior of these compounds in the
405 atmosphere using both, laboratory experiments and field measurements with a higher time
406 resolution to understand the physicochemical processes involved including gas to particle phase
407 conversion.

408

409

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416

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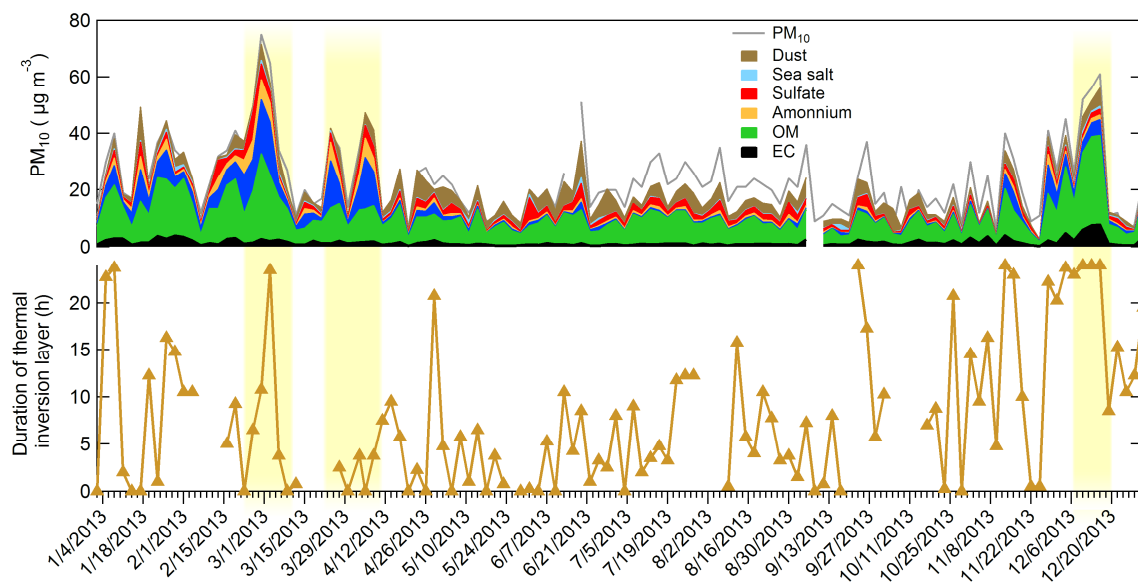


Figure Captions

Fig. 1. Annual trends (2013) of PM₁₀ concentrations (chemical composition, OM: organic matter = 1.8×OC) together with the duration of thermal inversion layer (h) at the urban background station of Grenoble-Les Frênes.

Fig. 2. Annual trends (2013) of total concentrations (gaseous and particulate phases) of phthalaldehyde, 1,2-naphthoquinone (only in gas phase), biphenyl-2,2'-dicarboxaldehyde (only in gas phase) and indeno[1,2,3-cd]pyrene at the urban background station of Grenoble-Les Frênes.

Fig. 3. Annual trends (2013) of the ratio [(2+3)-NFI]/[1NP] together with NO₃⁻, EC, levoglucosan and 1-nitropyrene (1-NP) in the particulate phase, at the urban background station of Grenoble-Les Frênes. Yellow shaded areas show the periods of severe PM pollution events.

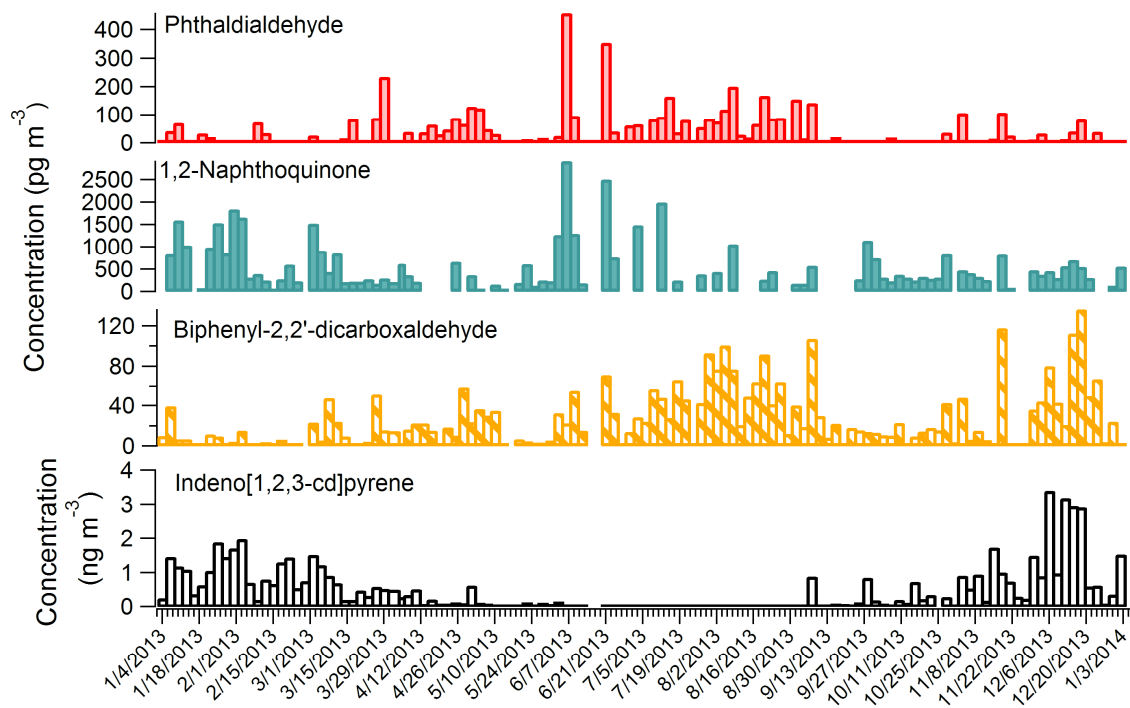
Fig. 4. Annual trends (2013) of (E)-2-formylcinnamaldehyde (2-FCin), 6H-dibenzo[b,d]pyran-6-one, 9-nitroanthracene, 1-naphthaldehyde and 1,8-naphthalic anhydride total concentrations together with NO at the urban background station of Grenoble-Les Frênes. Yellow tinted background areas show the periods of severe PM pollution events.

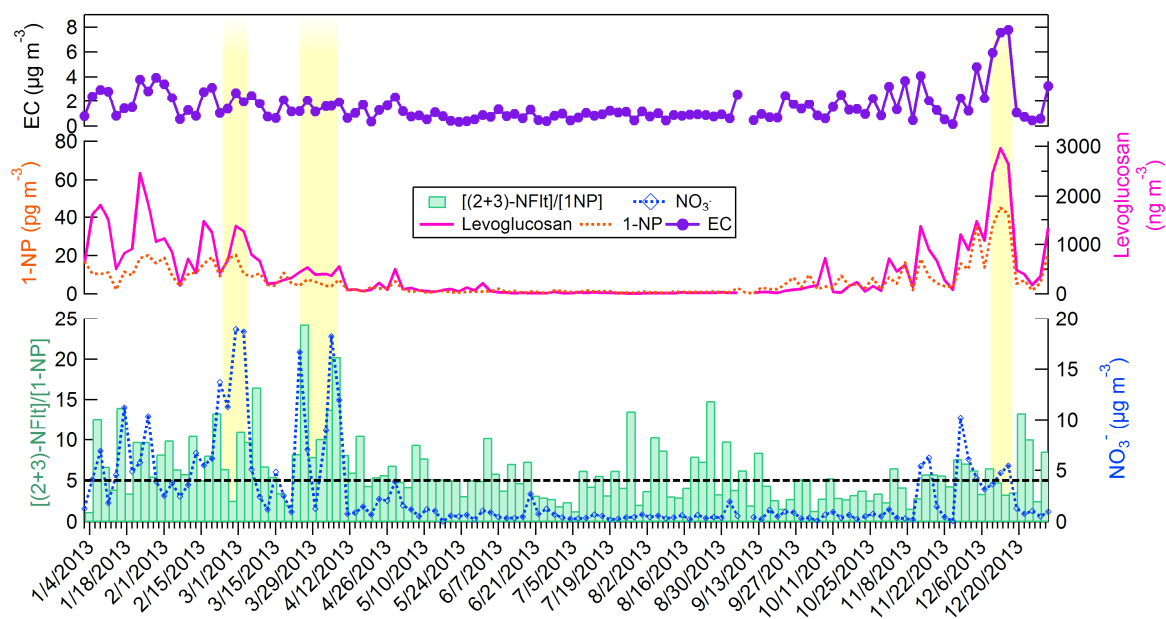
Fig. 5. Wind rose (km h⁻¹) (left) and NWR for PM₁₀ (µg m⁻³) (right) from the 02/25/2013 to the 03/06/2013 (A) and from the 12/09/2013 to the 12/19/2013 (B).

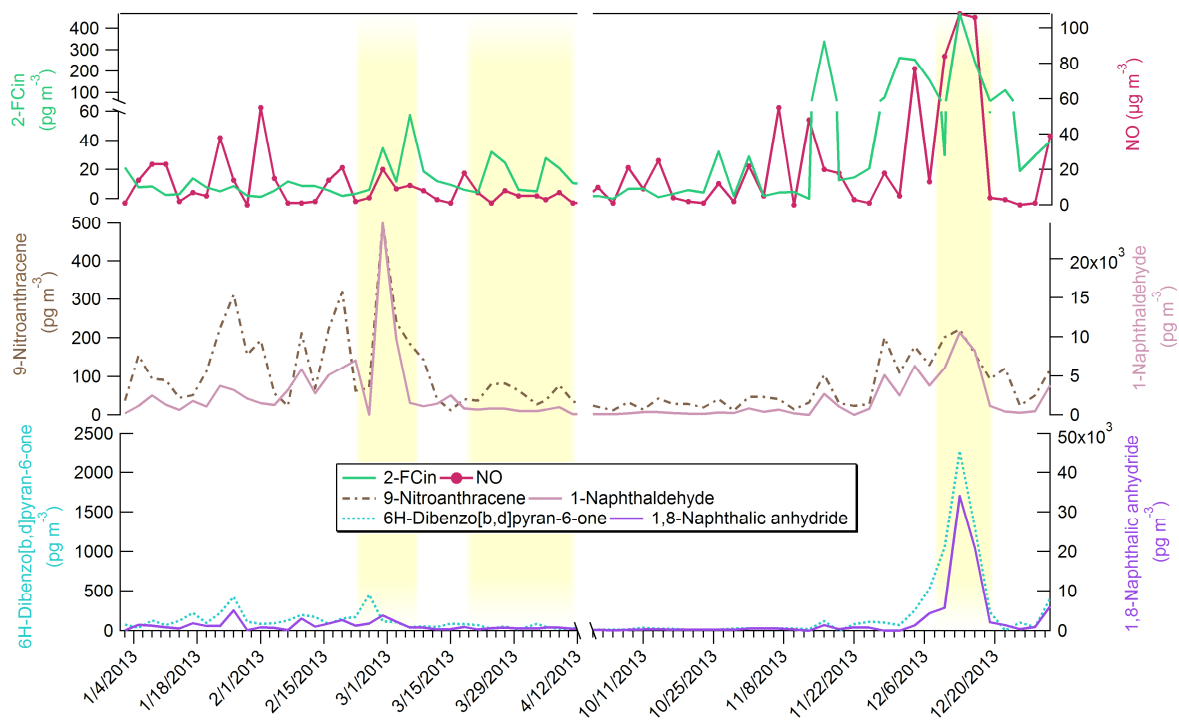
Fig. 6. Temporal evolution of (E)-2-formylcinnamaldehyde, phthalaldehyde and phthalic anhydride concentrations (in both gaseous and particulate phases) during the severe PM

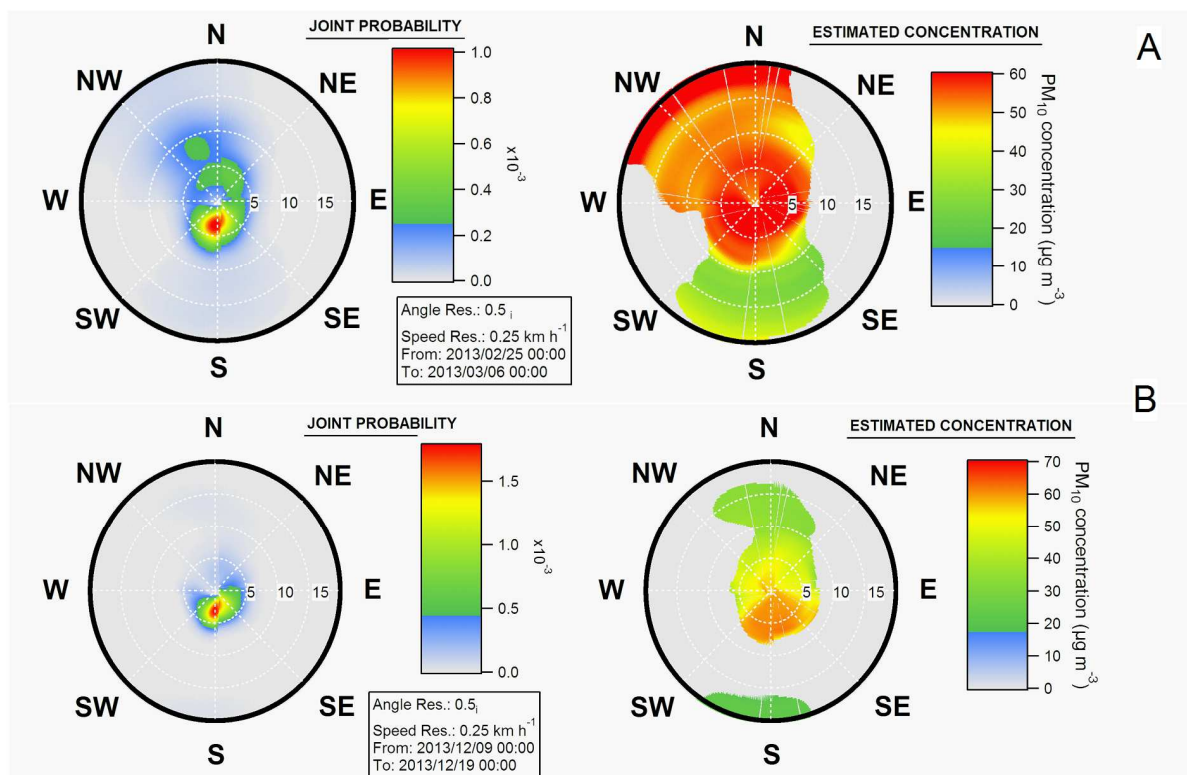
pollution event of December (12/09/2013 to 12/19/2013) at the urban background station of Grenoble-Les Frênes.

Fig. 7. Annual trends of the concentration ratios to their parent PAHs of 3-nitrophenanthrene ([3-NPhe]/[Phe]), 6H-dibenzo[b,d]pyran-6-one ([6H-DPone]/[Phe]), biphenyl-2,2'-dicarboxaldehyde ([Biph 2,2']/[Phe]), 9,10-anthraquinone ([9,10-ANQ]/[Anth]), benz[a]anthracene-7,12-dione ([B-7,12-D]/[B[a]A]), 1-nitropyrene ([1NP]/[Pyr]) together with (2+3)-nitrofluoranthene ([(2+3)-NFlt]/[1-NP]), O₃, EC and oxalate concentrations at the urban background site of Grenoble-Les Frênes. Gaseous and particulate phases are taken into account for all oxy- and nitro-PAHs except for biphenyl-2,2'-dicarboxaldehyde (only in gas phase).

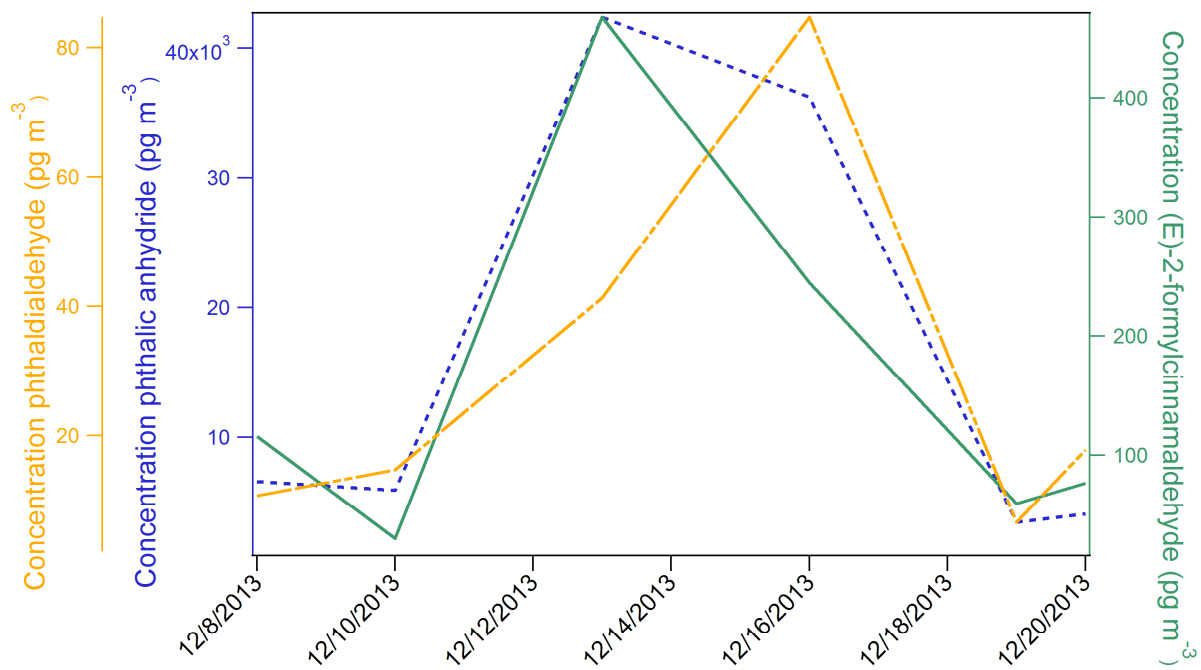


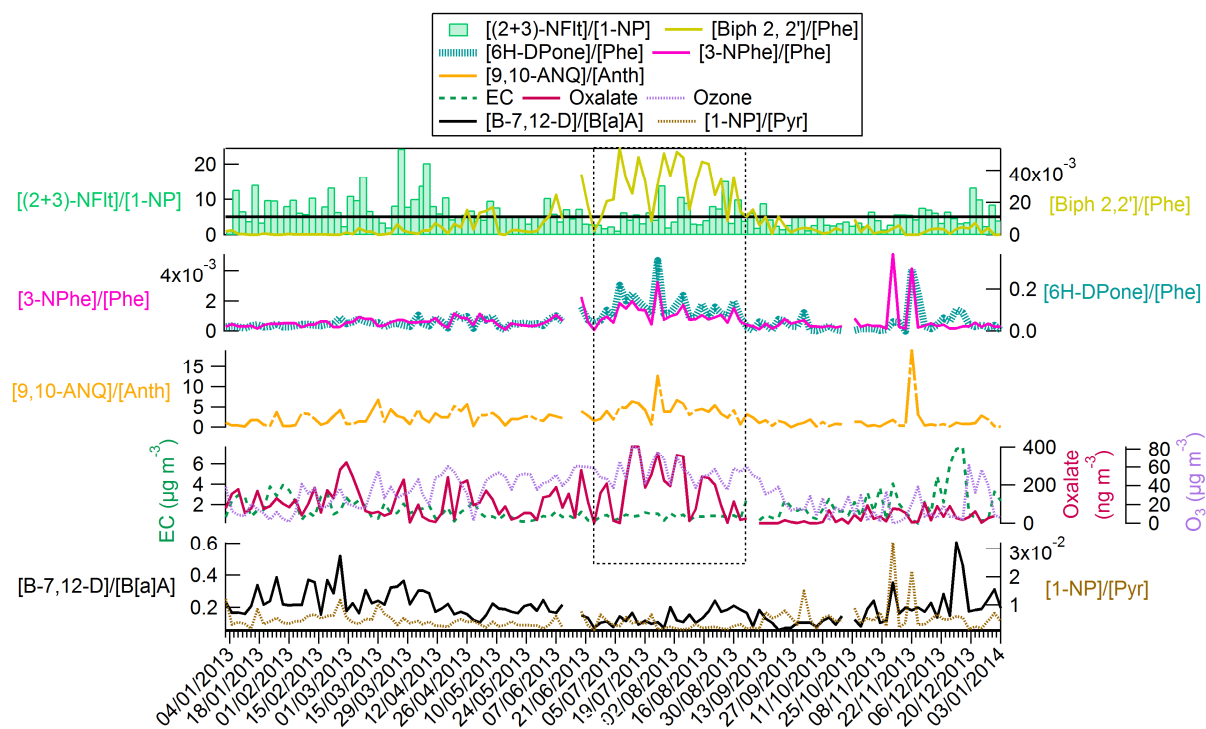






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PACs measured over a year together with an extended aerosol chemical characterization

Cold period was affected by primary emissions especially from residential heating

The highest (2+3)-NFlt/1-NP ratio was surprisingly observed during the winter period

Different secondary processes involved during the severe PM pollution events observed

Marker of PAH oxidation identified based on field observations and literature data