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

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Abstract

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

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

1. Introduction

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

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

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

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

2. Experimental

2.1 Sampling site

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

2.2 Sample collection

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

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

PM₁₀ (TEOM-FDMS, TEOM 1405F, Thermo), NO_x (TEI 42I, Thermo) and O₃ (TEI 49I, Thermo) concentrations were also monitored. Meteorological parameters (temperature, wind direction, wind speed) were measured by the local air quality network in Grenoble (Air Rhône-Alpes) and provided by ROMMA network (Meteorological network of the Alpine massif). Temperature and pressure data from several locations at different altitudes were used to evaluate the duration of thermal inversion layers in the Grenoble valley. Details are presented in the Supplementary Information A.

2.3. Analytical procedures

Anions (Cl⁻, NO₃⁻, SO₄²⁻), cations (NH₄⁺, Ca²⁺, Na⁺) and oxalate (C₂O₄²⁻) were analyzed by ion chromatography according to Jaffrezzo et al. (2005). Levoglucosan was quantified using HPLC-PAD (Waked et al., 2014) and EC /OC were measured using a Sunset lab analyzer using the EUSAAR-2 thermal protocol (Cavalli et al., 2010).

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

2.4. Quality assurance and quality control

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

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

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

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

3. Results and discussion

3.1. Overview of PM chemical composition and pollution events

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

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

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

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

Similarly to the first PM pollution event, a second event was observed in December, with PM_{10} concentrations about $56 \mu\text{g m}^{-3}$ on average and with a large contribution of organic matter (OM) to the total PM composition and the occurrence of thermal inversion layers over a long period (10 consecutive days).

3.2. Annual trends of individual compounds

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4. Conclusion

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

processes in ambient air.

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

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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 phthaldialdehyde, 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, phthaldialdehyde 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).

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