Atmospheric Environment 81 (2013) 561–568

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

One-year study of nitro-organic compounds and their relation to wood burning in PM_{10} aerosol from a rural site in Belgium

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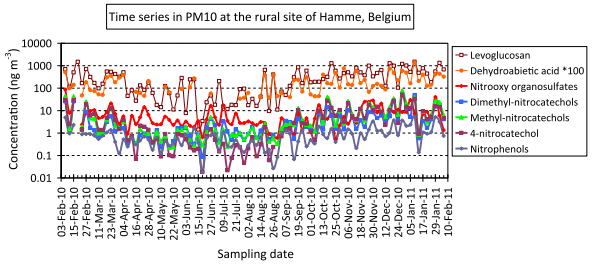
HIGHLIGHTS

- Nitro-aromatic compounds, α-pinene related organosulfates and a resin acid measured.
- Compounds measured in PM_{10} every 4th day over a full year at a rural site.
- Strong seasonality for most compounds, highest levels in winter, lowest in summer.
- Organosulfates pronounced in summer, but highest levels in winter.
- Nitro-aromatic compounds and the resin acid associated with wood burning.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 June 2013
Received in revised form
16 September 2013
Accepted 19 September 2013

Keywords:
Wood burning
Nitrocatechols
Nitrophenols
Nitrooxy-organosulfates
Atmospheric aerosol
HPLC/(−)ESI-ITMS
Resin acid

ABSTRACT

Nitro-organic compounds were determined in a one-year set of atmospheric PM_{10} filter samples that were collected at a rural background site in Hamme, Belgium. In an earlier study, it was found that the site was substantially impacted by wood burning, making the filter samples appropriate for further investigations on wood burning indicators. In total, four groups of nitro-aromatic compounds (with molecular weights (MWs) of 139, 155, 169, and 183), α-pinene-related nitrooxy-organosulfates (MW 295), and the resin acid dehydroabietic acid (DHAA, MW 300) were quantified using liquid chromatography combined with negative ion electrospray ionization mass spectrometry. The annual mean concentrations were 0.94, 6.0, 7.7, 4.8, 7.8, and 1.76 ng m^{-3} for the sum of the nitrophenols (MW 139), 4-nitrocatechol (MW 155), the sums of the methyl-nitrocatechols (MW 169), of the dimethyl-nitrocatechols (MW 183), and of the α-pinene-related nitrooxy-organosulfates (MW 295), and DHAA (MW 300), respectively. 4-nitrocatechol, the sum of the methyl-nitrocatechols, and the sum of the dimethyl-nitrocatechols were substantially correlated with levoglucosan (*r*-values of 0.71, 0.66, and 0.65, respectively), consistent with their proposed origin from biomass burning. The nitro-aromatic compounds were also observed during the summer months, indicating a non-negligible usage of wood burning for domestic purposes at the site. The α-pinene-related nitrooxy-organosulfates (MW 295) were detected in high concentrations during the winter period, but they were poorly correlated with the biomass burning tracers. All of the targeted species showed a clear seasonal variation with highest concentrations in winter, followed by autumn, spring, and summer. Based on the DHAA measurements, it is suggested that burning of softwood is likely an important source for the formation of all the nitro-organic compounds measured.

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http://dx.doi.org/10.1016/j.atmosenv.2013.09.041

1. Introduction

Biomass burning, including the combustion of wood, is often used for heating and cooking purposes and in agricultural practices. It releases a substantial amount of particulate matter (PM), trace gases such as CO, CO_2, CH_4, NO_x, non-methane hydrocarbons, oxygenated compounds, and others into the atmosphere (e.g., Andreae and Merlet, 2001; Simoneit, 2002; Lemieux et al., 2004) and has raised serious concerns for its effects on local and regional air quality, human health, and climate. The combustion of wood for heating is an inexpensive practice and might become more popular as it is also a renewable energy source. Problems arise as wood stoves and fireplaces typically emit much more particles than other heating devices. Depending on the combustion conditions and the type of wood/material burned, the emissions of gases and particles may vary a lot. In the future, it is likely that environmental policies will address residential wood burning to reduce air pollution, as is currently already done in some states of the US (e.g., in California) and also in Belgium.

Biomass burning aerosol (BBA) can contribute from 3 to 14% to the annual mean PM_{10} level in Europe (Gianini et al., 2012; Maenhaut et al., 2012; Reche et al., 2012), but depending on the sampling site, season, and meteorological conditions, the contribution can show substantial variation. For example, Yttri et al. (2009) found that wood burning accounted for 46–83% of the PM_{10} mass at Norwegian sites in winter. Previous research suggests that rather individual parameters such as the number of ultrafine particles, bioavailability of transition metals, polycyclic aromatic hydrocarbons, and other particle-bound organic species are likely more important than the particle mass concentration with respect to the health effects of combustion aerosols (Lighty et al., 2000).

In this context, nitro-aromatic compounds and, in particular, methyl-nitrocatechols have drawn increasing attention in recent years. A strong correlation of methyl-nitrocatechols with levoglucosan ($r = 0.87$), a primary tracer compound for biomass burning, indicated that the methyl-nitrocatechols likely originate from the same source as levoglucosan, i.e., biomass burning (Iinuma et al., 2010). Furthermore, methyl-nitrocatechols have been suggested as tracers for processed (aged) BBA, as they are formed from the further oxidation of volatile organic compounds that are emitted upon biomass burning, including aromatic compounds such as *m*-cresol (Iinuma et al., 2010). Several other nitro-aromatic compounds were observed in urban aerosol samples, including nitrophenols, 4-nitrocatechol, methyl homologs of methylnitrocatechols, nitroguaiacols, and nitrosalicylic acid (Kitanovski et al., 2012a,b). Since these compounds have a low molecular weight and contain one or more hydroxyl groups, they are mainly present in the hydrophilic fraction of atmospheric particulate matter. Furthermore, nitro-aromatic compounds can absorb light in the UV/VIS range and, hence, their fraction in atmospheric aerosol might contribute to the effect of aerosols on the solar radiation balance. In this respect, nitro-aromatic compounds have been shown to be present in HULIS samples and to correspond to their yellow-colored substances (Claeys et al., 2012).

As they are likely toxic compounds (Arey et al., 1988; Harrison et al., 2005), nitro-aromatic compounds should be further characterized and quantified in atmospheric aerosol samples to better understand their sources and processes in the atmosphere and to better assess their impact for air quality issues.

The objectives of the present study were to gain more insights into BBA and the nitro-organic compounds by analyzing rural background PM_{10} aerosol samples that were collected over a full year, considering that most studies on atmospheric nitro-aromatic compounds were limited to a certain period of the year. In the present investigation, α-pinene-derived nitrooxy-organosulfates (with molecular weight (MW) of 295), which are related to biogenic precursors, were measured as well. The latter nitrooxy-organosulfates have been shown to peak during nighttime in $PM_{2.5}$ samples collected at a forested site in Brasschaat, Belgium, during summer (Gómez-González et al., 2012). A puzzling feature is their recent observation in winter aerosol samples collected at an urban background site in Aarhus, Denmark (Hansen et al., 2012), where monoterpene emission is expected to be rather low. Different mechanisms were suggested to explain the formation of the α-pinene-related MW 295 nitrooxy-organosulfates, including photo-oxidation of α-pinene in the presence of NO_x or its oxidation through NO_3 radical reactions (Surratt et al., 2008). A possible explanation for their presence in summer nighttime and winter aerosol samples is that their intermediates, the pinanediol nitrates, need a lower temperature to partition to the particle phase (Aschmann et al., 1998; Surratt et al., 2008), where they are subsequently sulfated. Therefore, we considered it worthwhile to target the MW 295 nitrooxy-organosulfates in the present study to derive possibly additional information from an annual data set.

In a recent study on wood burning in Flanders, Belgium, whereby PM_{10} filter samples collected at seven sites over the year 2010–2011 were analyzed, it was found that the rural site of Hamme was substantially more impacted by biomass burning than the other six sites (VMM, 2011; Maenhaut et al., 2012). A major organic component in BBA is levoglucosan, which is a known primary tracer for biomass burning that forms during the pyrolysis of cellulose (Simoneit et al., 1999). It is often observed together with additional anhydrosugars such as mannosan and galactosan, which result from the pyrolysis of hemicelluloses. These additional anhydrosaccharides are usually detected as minor constituents compared to levoglucosan (Nolte et al., 2001). High concentrations of monosaccharide anhydrides, i.e., levoglucosan, mannosan, and galactosan, were observed at the site in Hamme (Maenhaut et al., 2012). The annual average contributions from wood burning to the organic carbon in PM_{10} and the PM_{10} mass were 36% and 13.3%, respectively, making the samples from this site of interest for further investigations on BBA. The aim of the present study was to examine the impact of wood burning on individual organic compounds, including nitro-aromatic compounds, nitrooxy-organosulfates, and the resin acid dehydroabietic acid (DHAA) over a one-year time period. DHAA (MW 300), a tricyclic diterpene carboxylic acid, was considered as it is specific for softwood burning and has been suggested as a suitable tracer for the latter process (Simoneit et al., 1993; Standley and Simoneit, 1994). The detection of this compound can thus provide valuable information about the burned wood type as soft- and hardwood can be differentiated (Fine et al., 2001, 2002).

2. Experimental

2.1. Aerosol collection

PM_{10} filter samples were collected according to EN 12341 (1999) at a rural background site (51°5′36″N, 4°6′32″E, 4 m a.s.l.) in Hamme, Flanders, Belgium. The site was expected to be strongly impacted by wood burning, as there are several inhabitants in the neighborhood, who use wood as fuel (Maenhaut et al., 2012). A low-volume filter sampler SEQ 47/50 (Leckel GmbH, Berlin, Germany) was used and 24-h samples (with filter change at 23:55 UT) were taken every 4th day from 7 February 2010 until 6 February 2011. The sampler was operated at 2.3 $m^3\ h^{-1}$ and 47-mm diameter Pallflex® Tissuquartz™ 2500 QAT-UP quartz filters (PALL Corp., NY, USA), which were preheated in the factory, were used. The aerosol deposit area was 11.64 cm^2 and the air volume per sample was 55.1 m^3. In total 92 filter samples and 9 field blank samples were

taken, whereby for the latter ones no air was drawn through the filter. All filter samples were stored in a freezer below −18 °C until analysis.

2.2. Filter analysis

The filters were analyzed in a previous study (Maenhaut et al., 2012) for the PM mass, organic, elemental, and total carbon (OC, EC, and TC), and 3 anhydrosugars (levoglucosan, mannosan, and galactosan). Based on the results from the levoglucosan analysis, the filter samples were divided into two groups in the present investigation. Filters containing less than 1 μg levoglucosan per 1 cm^2 were considered as lowly loaded filters and 2 cm^2 was taken from them for further analysis, whereas the filters containing more were considered as highly loaded ones and 1.5 cm^2 was used. Two internal recovery standards were added to the filter pieces to correct for losses and possible errors during the sample preparation; these standards were the commercially available compounds 3-nitrophenol (99%, Sigma–Aldrich, St. Louis, MO, USA) and sodium decyl sulfate (HPLC grade, Acros Organics, Belgium). An absolute amount of 5 ng of each compound was added to the 2 cm^2 filter pieces and of 10 ng to the 1.5 cm^2 pieces. The filter pieces were extracted three times with 10 mL methanol (ULC MS grade, Biosolve, Valkenswaard, The Netherlands) under ultrasonic agitation for 5 min. The combined extracts were concentrated using rotary evaporation (30 °C, 100 mbar) and the resulting solution was filtered using a PTFE syringe filter with a diameter of 0.45 μm (Grace Davison Discovery Sciences, Deerfield, IL, USA) and the filtrate was dried using a gentle stream of nitrogen. The dried extracts were stored in a refrigerator and reconstituted in 100 μL water just before analysis.

2.3. Quantification of the target compounds

The nitro-organic compounds with *m*/*z* values of 138, 154, 168, 182, and 294 were quantified in this study using different authentic or surrogate standards by means of an internal calibration method. For the nitrophenols (*m*/*z* 138) 4-nitrophenol (spectrophotometric grade, Fluka) served as authentic standard and for 4-nitrocatechol (*m*/*z* 154) the same compound (97%, Sigma–Aldrich), whereas for the detected methyl-nitrocatechol isomers (*m*/*z* 168) and dimethyl-nitrocatechols (*m*/*z* 182) the commercially available 4-methyl-5-nitrocatechol (Santa Cruz Biotechnology Inc., USA) was used. For all of these species, the ratio was calculated of the peak area of the target compound to the peak area for the internal recovery standard 3-nitrophenol (99%, Sigma–Aldrich). The nitrooxy-organosulfates (*m*/*z* 294) were determined using sodium octyl sulfate (*m*/*z* 209) (HPLC grade, Merck, Germany) as a surrogate standard, as no authentic standard was available for the *m*/*z* 294 compounds. For these targeted species, the ratio between the *m*/*z* 294 signal (and for the standard the *m*/*z* 209 signal) and the *m*/*z* 237 signal of deprotonated decyl sulfate (HPLC grade, Acros Organics, Belgium), the internal recovery standard for organosulfates, was calculated. The surrogate and recovery standards for the organosulfates were the same as used in previous work of our laboratory (Gómez-González et al., 2012) and were chosen for the present work owing to their retention times (RTs), e.g., being 21.7 min for the surrogate standard, and thus close to the RTs of the targeted organosulfates.

In addition to the nitro-organic compounds also resin acids such as DHAA (MW 300) and pimaric acid (MW 302) were detected. Although the analytical procedure was not optimized for those species, an effort was made to quantify the most abundant compound, DHAA. The DHAA standard was purchased from the CanSyn Chemical Corporation (Toronto, Canada) in >99% purity. Estimation of the extraction recovery of DHAA was done by spiking Pallflex quartz fiber filter sections of 1.5 cm^2 with known amounts of DHAA, subjecting the sections to the same filter analysis procedure as for the actual samples, and comparing the peak area for DHAA in these sections with that for a DHAA standard solution. An average extraction recovery of 95% was obtained.

The concentrations in the standard solutions ranged from 0.005 to 4 μg mL^{-1}, with up to 10 concentrations (equally spaced on a logarithmic scale). For 4-nitrophenol, 4-nitrocatechol, 4-methyl-5-nitrocatechol, octyl sulfate, and dehydroabietic acid, weighted quadratic calibration curves (using $1/y^2$ weighing) were constructed using SPSS (20.0.0). The calibration curve for octyl sulfate extended over the entire concentration range, but for the other standard compounds, separate calibration curves were constructed for a low and high concentration range, whereby the curves for the low concentration range were forced through the origin.

2.4. Analytical method

Liquid chromatography/mass spectrometry (LC/MS) analysis was performed using a Surveyor Plus system (pump and autosampler) (Thermo Scientific, San Jose, USA) connected to a linear ion-trap mass spectrometer (LXQ, Thermo Scientific), which has unit mass resolution. A Hypersil Gold column (2.1 × 150 mm; 3 μm) (Thermo Scientific, San Jose, USA) was employed for the chromatographic separation of the targeted compounds using an acetonitrile gradient. The mobile phases consisted of a 50 mM ammonium formate buffer pH 3 (A) and acetonitrile (B). The buffer was prepared by dissolving ammonium formate (>99%, MS grade, Sigma–Aldrich) in Milli-Q water and adding formic acid (pro analysis, 98–100%, Merck KGaA, Darmstadt, Germany) until the pH value was 3. The following 65 min program was applied during the LC analysis: eluent B was kept at 3% for 5 min, then increased to 95% in 15 min, kept at 95% for 25 min, decreased back to 3% in 10 min, and conditioned at 3% for 10 min for the following analysis. Samples were injected with an injection volume of 10 μL and the analysis was carried out using a flow rate of 0.2 mL min^{-1}.

2.5. Mass spectrometry

The targeted compounds were ionized using electrospray ionization in the negative mode. The mass spectrometer was operated under the following conditions: sheath gas flow (nitrogen), 50 arbitrary units; auxiliary gas flow (nitrogen), 5 arbitrary units; source voltage, −4.5 kV; capillary temperature, 350 °C; and maximum ion injection time, 200 ms. The $[M - H]^-$ signal optimization was done by direct injection of a 50 μg mL^{-1} *cis*-pinonic acid standard solution. The instrument was operated in the full scan mode over the mass range *m*/*z* 50–800. Extracted ion chromatographic (EIC) data were used to determine the peak areas of the targeted compounds, internal standards, and surrogate standards, which served as input data for the quantitative determinations.

For the unambiguous identification of dehydroabietic acid from the ambient filter samples, also MS^2 characterization was performed. Therefore, an isolation width of 2 *m*/*z* units and a normalized collision energy level of 35% were applied and the fragmentation patterns of the authentic standard and the peak detected in the filter samples at the same retention time as for the authentic standard were compared.

3. Results and discussion

The compounds determined in the present study had the following *m*/*z* values: *m*/*z* 138 (nitrophenols), *m*/*z* 154 (4-

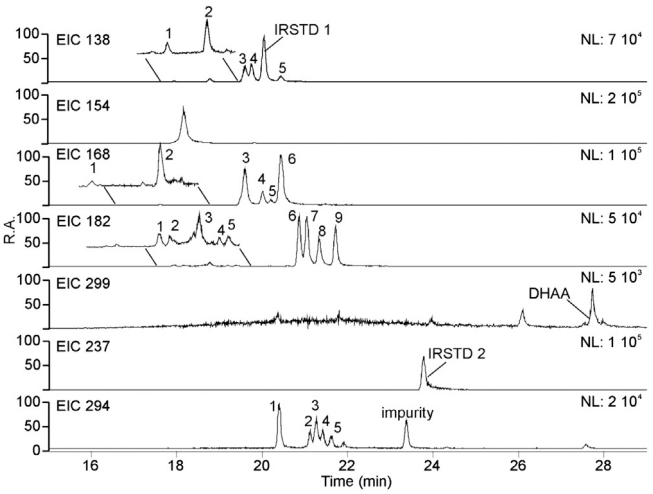

Fig. 1. Extracted Ion Chromatograms (EICs) at m/z values of the deprotonated molecules of the compounds quantified in this study: m/z 138 (nitrophenols), m/z 154 (4-nitrocatechol), m/z 168 (methyl-nitrocatechols), m/z 182 (dimethyl-nitrocatechols), m/z 294 (pinanediol nitrooxy-organosulfates), and m/z 299 (dehydroabietic acid). Abbreviations: IRSTD, internal recovery standard; DHAA, dehydroabietic acid; and NL, normalization level. The isomers are indicated by numbers. Note that the number of isomers with peaks above detection limit was less than the possible maximum number of 6, 7 and 11 for the nitrophenols, methyl-nitrocatechols, and dimethyl-nitrocatechols, respectively.

nitrocatechol), m/z 168 (methyl-nitrocatechols), m/z 182 (dimethyl-nitrocatechols), m/z 294 (nitrooxy-organosulfates) and a resin acid m/z 299 (DHAA). A typical chromatogram from a highly loaded PM_{10} filter sample is shown in Fig. 1. As can be seen from the EICs, all the targeted compounds, with the exception of that with m/z 154, exhibited several isobaric isomers; for the nitrophenols there were up to 6 isomers, for the methyl-nitrocatechols up to 7, for the dimethyl-nitrocatechols up to 11, and for the nitrooxy-organosulfates 5. The isomers include positional isomers of the nitro- and/or methyl-groups but may also correspond to other structures. For example, the m/z 168 isomers can be attributed to positional isomers of methyl-nitrocatechols, but also of nitroguaiacols. As only a limited number of possible isomers is commercially available, the exact chemical assignment of unknowns in the atmospheric aerosol samples is mostly tentative. Based on comparison with literature data (Kitanovski et al., 2012b), the two major m/z 168 peaks (RT 19.5 and 20.5 min) were assigned to 4-methyl-5-nitrocatechol and 3-methyl-5-nitrocatechol, whereas an additional peak with low intensity (RT 19.9 min) is tentatively assigned to 6-nitroguaicaol. The concentrations of these three compounds accounted, on average, for 43%, 31%, and 3% of the sum of the 7 methyl-nitrocatechols.

The time series for the nitro-organic compounds in the PM_{10} aerosol samples from Hamme over the whole year 2010–2011 is shown in Fig. 2. The most prominent compounds are 4-nitrocatechol (MW 155) and the methyl-nitrocatechols (MW 169), which is in agreement with previous studies (Iinuma et al., 2010; Kitanovski et al., 2012b). Also nitrooxy-organosulfates (MW 295), which are related to α-pinene, were observed during the whole year. The time courses of all compounds point to sources over the whole year. Nevertheless, all compounds show a clear seasonal variation with largest levels in winter, followed by autumn, spring, and summer (Table 1); the anhydrosugars showed a similar seasonal variation (Maenhaut et al., 2012; and Table 1). Table 1 shows that, for most compounds, the median concentration is more than an order of magnitude higher in winter than in summer. This is especially the case for the MW 155 and 169 compounds. Elevated concentrations for the latter compounds in wintertime aerosol were already observed in previous studies from smaller data sets and it was proposed that these compounds originated from biomass burning, based on their correlation with levoglucosan (Iinuma et al., 2010; Kitanovski et al., 2012a). Correlations were also calculated between the various compounds measured in the current study and the data obtained by Maenhaut et al. (2012); the results are presented in Table 2. The nitro-aromatic compounds are highly correlated among each other with r-values larger than (or equal to) 0.76. Especially, 4-nitrocatechol (MW 155) and the sums of its methyl-analogs (MWs 169 and 183) were very highly correlated with each other (all r-values > 0.9), suggesting similar sources or source processes. The nitro-aromatic compounds were also substantially correlated with levoglucosan ($r > 0.5$), suggesting that they are related to biomass burning. A possible source of 4-nitrocatechol is the photo-oxidation of benzene (Borras and Tortajada-Genaro, 2012), which could also have other sources than biomass burning, such as traffic exhaust. However, taking into account the results of the correlation analysis, it is likely that most of the benzene, which acted as precursor for 4-nitrocatechol in the present study, is emitted by biomass burning, as this process is an important source of benzene (Andreae and Merlet, 2001). Also OH oxidation of phenol has been shown to lead to nitrophenols (e.g., Yee et al., 2013; Olariu et al., 2002; Berndt and Böge, 2003), but only the formation of 3-nitrocatechol (and not of 4-nitrocatechol) has been reported so far (Berndt and Böge, 2003). Correlations between the nitro-aromatic compounds and levoglucosan were also calculated for the separate winter and summer seasons. While the correlation coefficients were all between 0.5 and 0.7 for winter, only 4-nitrocatechol was substantially correlated with levoglucosan, with $r = 0.50$ for the summer samples. This may indicate that the nitro-aromatic compounds can have also other sources besides biomass burning in summer.

The major MW 169 compounds were recently identified as methyl-nitrocatechols and were shown to originate from m-cresol OH reactions in the presence of NO_x (Iinuma et al., 2010). Since m-cresol is released during wood combustion as a thermal degradation product of lignin, methyl-nitrocatechols have been suggested as tracers for biomass burning secondary organic aerosol that forms likely in secondary oxidation steps during the processing of BBA. Also the photo-oxidation of anthropogenic VOCs such as toluene can certainly lead to the MW 169 compounds (Jang and Kamens, 2001; Huang et al., 2006). Like is the case for benzene, also toluene is in substantial amounts emitted by biomass burning (Andreae and Merlet, 2001). The summed concentration of the measured nitro-aromatic compounds (MWs 139, 155, 169, and 183), expressed as percentage of the OC concentration in PM_{10}, for the winter samples ($n = 22$) was 0.75%, a value which is in excellent agreement with that obtained by Kitanovski et al. (2012a) for PM_{10} aerosol in winter (i.e., 0.79%, $n = 15$) at an urban background location in Ljubljana, Slovenia.

It is noteworthy that the MW 295 nitrooxy-organosulfates were also detected in high concentrations in winter in the present study. Although the existence of these nitrooxy-organosulfates, which are related to α-pinene (Surratt et al., 2008), was recently also reported for winter samples from Denmark (Hansen et al., 2012), their origin and their formation mechanism during the winter months remain speculative, as the emission of the biogenic precursor compounds is rather low during this period of the year (Hakola et al., 2012). It was found for a summer campaign at a forested site in Brasschaat, Belgium (Gómez-González et al., 2012) that the MW 295 particle phase concentrations peaked during nighttime, when temperatures were low. It remains, however, uncertain whether this observation is related to an enhanced partitioning of the MW 295 precursor compounds, the pinanediol nitrates, to the aerosol phase

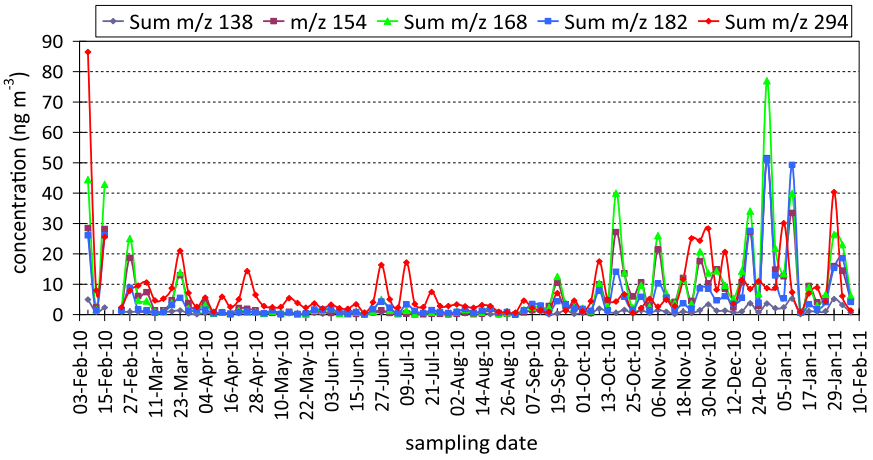

Fig. 2. Time series of the nitro-organic compounds over the year 2010–2011 in PM_{10} at Hamme, Belgium.

(Aschmann et al., 1998; Surratt et al., 2008). The occurrence of MW 295 compounds in nighttime SOA has also been reported by Iinuma et al. (2007). Considering that the highest concentrations of the MW 295 nitrooxy-organosulfates were observed in winter in the present study, when also the wood burning indicators, exhibited their highest levels, it is of interest to examine the correlation between the various compounds. It appears from Table 2 that the correlation coefficients of the nitrooxy-organosulfates with the anhydrosugars and with the nitro-aromatic compounds are all lower than 0.5, with the exception of that between the nitrooxy-organosulfates and the nitrophenols, which is 0.64. These overall poor correlations seem to suggest that it is rather unlikely that the MW 295 compounds are formed during or associated with the combustion of wood. However, it has been found that α-pinene is emitted from boreal forest fires (Simpson et al., 2011) and also from wood burning in fireplaces, be it that the emission levels are much lower than those from active prescribed burning (Lee et al., 2005). Cheng et al. (2011) suggested that the α-pinene is emitted from burning softwood logs in domestic fireplaces and/or stoves. As indicated below, softwood burning is important in Flanders. Thus, the high levels of the MW 295 nitrooxy-organosulfates in winter might after all well be associated with wood burning. Our summer median of 2.8 ng m^{-3} for the organosulfates is fairly similar to, but clearly larger than the median of 1.51 ng m^{-3} that was observed by Gómez-González et al. (2012) during a 2007 summer campaign at the forested site of Brasschaat, Belgium. This may indicate that even in summer a substantial fraction of the organosulfates in Hamme originates from wood burning.

DHAA represents a specific compound that can be detected in smoke of coniferous wood or softwood (Simoneit et al., 1993; Standley and Simoneit, 1994). In the present study, this tricyclic diterpene acid was observed throughout the whole year, whereas another resin acid, pimaric acid (MW 302), was only present in low abundance in a few samples. Based on the comparison of the chromatographic behavior and of the MS^2 product ion spectrum with those of an authentic standard, DHAA was unambiguously identified in the samples (Fig. 4). Our DHAA concentrations are in good agreement with published values for a residential site in southern Germany (Bari et al., 2009), but they are about an order of magnitude lower than those reported by Kubátová et al. (2002) for an urban background site in Gent, Belgium. Although the DHAA concentration was rather low or below the detection limit in the summer samples, it exhibited a clear seasonal trend (summer < spring < autumn < winter). DHAA was highly correlated with levoglucosan and the other two anhydrosugars (all *r*-values ≥ 0.78). The good correlation between DHAA and levoglucosan can clearly be seen in Fig. 3.

The average DHAA/levoglucosan ratio over all our samples was 0.0059 ± 0.0079 (0.0057 ± 0.0040 for the winter samples only). This ratio can be compared with the DHAA/levoglucosan ratios, obtained by Bari et al. (2010) of 0.00048 for hardwood (beech) and 0.0021 for softwood (pine) smoke, respectively, and such

Table 1
Overall and seasonal median concentrations and interquartile ranges for the PM mass, OC, and EC (all in μg m^{-3}) and for levoglucosan, mannosan and galactosan, the nitro-organic compounds, and DHAA (all in ng m^{-3}). The data for the PM mass, OC, EC, and the anhydrosugars were taken from Maenhaut et al. (2012).

	Overall	Spring	Summer	Autumn	Winter
	Median (25%–75%)	Median (25%–75%)	Median (25%–75%)	Median (25%–75%)	Median (25%–75%)
PM mass [μg m^{-3}]	26 (19.1–34)	29 (24–37)	19.5 (17.2–24)	24 (18.9–31)	32 (26.2–52.2)
OC [μg m^{-3}]	4.0 (2.9–5.8)	3.7 (2.5–4.4)	3.3 (20–42)	4.5 (3.6–5.7)	5.9 (3.2–9.0)
EC [μg m^{-3}]	0.63 (0.42–0.82)	0.49 (0.37–0.73)	0.44 (0.38–0.54)	0.77 (0.67–1.0)	0.77 (0.42–1.00)
Levoglucosan [ng m^{-3}]	200 (58–510)	124 (54–300)	18.1 (13.7–93)	340 (193–550)	640 (460–1010)
Mannosan [ng m^{-3}]	34 (10.5–82)	21 (9.4–46)	3.2 (2.1–15.6)	52 (31–114)	88 (69–124)
Galactosan [ng m^{-3}]	11.3 (3.5–29)	8.0 (3.8–18.3)	0.93 (0.64–4.0)	18.7 (9.8–31)	33 (20–48)
NP ($\sum m/z$ 138) [ng m^{-3}]	0.65 (0.32–1.03)	0.51 (0.30–0.67)	0.29 (0.17–0.62)	0.91 (0.45–1.39)	1.19 (0.92–3.0)
4-NC (m/z 154) [ng m^{-3}]	1.91 (0.49–9.0)	1.37 (0.52–3.0)	0.23 (0.09–0.42)	4.7 (2.7–10.5)	11.6 (4.2–18.0)
MNC ($\sum m/z$ 168) [ng m^{-3}]	2.2 (0.86–9.3)	1.07 (0.61–1.88)	0.77 (0.45–1.23)	3.7 (2.4–12.1)	13.9 (6.3–26.0)
DMNC ($\sum m/z$ 182) [ng m^{-3}]	1.66 (0.83–4.3)	0.83 (0.55–1.61)	0.87 (0.52–1.73)	3.4 (1.56–5.9)	5.5 (3.6–17.8)
NOS ($\sum m/z$ 294) [ng m^{-3}]	4.6 (2.5–8.3)	5.0 (2.5–6.8)	2.8 (2.2–3.4)	4.6 (2.2–6.9)	8.3 (6.3–11.3)
DHAA (m/z 299) [ng m^{-3}]	1.00 (0.39–2.4)	0.65 (0.00–1.49)	0.00 (0.00–0.51)	1.51 (0.64–2.4)	2.2 (1.41–4.7)

Abbreviations: NP, nitrophenols; 4-NC, 4-nitrocatechol; MNC, methyl-nitrocatechols; DMNC, dimethyl-nitrocatechols; NOS, nitrooxy-organosulfates.

Table 2
Correlation coefficients between the atmospheric concentrations of the PM mass, OC, EC, DHAA, the anhydrosugars, and the nitro-organic compounds. The data for the PM mass, OC, EC, and the anhydrosugars were taken from Maenhaut et al. (2012). Correlation coefficients larger than 0.7 are indicated in bold and values between 0.5 and 0.7 are in italic.

	PM mass	OC	EC	Levo	Manno	Galac	DHAA	NP	4-NC	MNC	DMNC	NOS
PM mass	1											
OC	**0.72**	1										
EC	0.45	0.58	1									
Levo	0.37	**0.78**	0.42	1								
Manno	0.27	**0.71**	0.43	**0.93**	1							
Galac	0.41	**0.80**	0.47	**0.97**	**0.96**	1						
DHAA	0.28	*0.61*	0.42	**0.78**	**0.78**	**0.80**	1					
NP	*0.59*	**0.73**	0.49	*0.57*	0.48	*0.62*	*0.54*	1				
4-NC	0.43	*0.68*	0.48	**0.71**	*0.60*	**0.74**	*0.56*	**0.76**	1			
MNC	0.44	*0.65*	0.42	*0.66*	*0.52*	*0.67*	*0.52*	**0.76**	**0.98**	1		
DMNC	0.44	*0.66*	0.46	*0.65*	*0.54*	*0.67*	*0.62*	**0.82**	**0.91**	**0.93**	1	
NOS	*0.65*	*0.60*	0.22	0.26	0.21	0.34	0.21	*0.64*	0.45	0.47	0.38	1

Abbreviations: Levo, levoglucosan; Manno, mannosan; Galac, galactosan; NP, nitrophenols; 4-NC, 4-nitrocatechol; MNC, methyl-nitrocatechols; DMNC, dimethyl-nitrocatechols; NOS, nitrooxy-organosulfates.

comparison seems to indicate that softwood burning prevails at our site. On the other hand, from the mean DHAA and levoglucosan concentrations obtained by Bari et al. (2010) for the ambient air of their rural residential area in southern Germany, one can derive a DHAA/levoglucosan ratio of 0.0048, and, although this ratio is higher than their emission ratio for softwood, the authors concluded by using multiple wood smoke tracer compounds that hardwood combustion is predominant in their area. The high correlation of the anhydrosugars with DHAA and, perhaps to a lesser extent, the DHAA/levoglucosan ratio suggest that the biomass burning aerosol at our site originates to a large extent from softwood burning. This was also concluded by Maenhaut et al. (2012), who used the levoglucosan/mannosan ratio to estimate the relative importance of softwood and hardwood burning for their seven measurement sites, including Hamme, in Flanders. It was found in the latter study that the contribution from softwood burning was about 70% and that it exhibited little variation with season or from site to site.

A previous study indicated that DHAA might not be stable in aqueous media when it is exposed to UV light (Corin et al., 2000). This could be of atmospheric relevance, especially for the samples collected during the summer period. Besides being highly correlated with the anhydrosugars, DHAA was also substantially correlated with all nitro-aromatic compounds (r-values from 0.52 to 0.62). Since DHAA is specific to softwood burning, it would be of interest to examine the relationship between DHAA and the anhydrosugars and the nitro-aromatic compounds (e.g., in terms of concentration ratios) at other sites that are either highly or very little impacted by softwood burning (or in smoke from wood stove combustion experiments), to find out whether a better discrimination between softwood and hardwood burning can be made than on the basis of the levoglucosan/mannosan ratio alone.

4. Summary and conclusion

The concentrations of nitro-aromatic compounds, nitrooxy-organosulfates, and the resin acid DHAA in PM_{10} aerosol were determined over a full year for a rural background site in Hamme, Belgium, which was known to be particularly impacted by biomass burning. The concentrations of the PM_{10} mass, OC, EC, and the three anhydrosugars levoglucosan, mannosan, and galactosan, in the samples from the Hamme site were available from a previous study (Maenhaut et al., 2012). Like was the case for the anhydrosugars, also the compounds measured in the current study exhibited a clear seasonal variation, with highest levels in winter, followed by autumn, spring, and summer. The summed concentrations of the measured nitro-aromatic compounds (MWs 139, 155, 169, and 183) and of the anhydrosugars, expressed as percentage of the OC concentration in PM_{10}, for the winter samples ($n = 22$) were 0.75% and 13.0%, respectively; these values are very similar to those obtained by Kitanovski et al. (2012a) for PM_{10} aerosol in winter (i.e., 0.79%

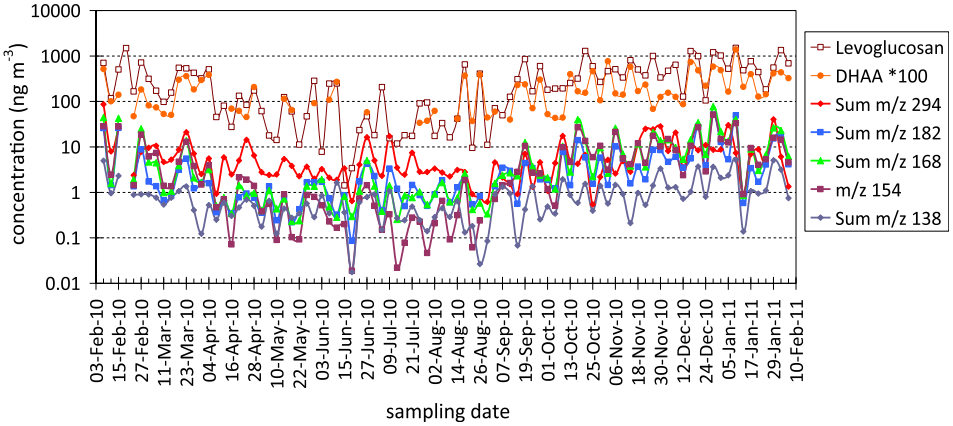

Fig. 3. Time series for all quantified organic compounds (shown with logarithmic ordinate scale) in the PM_{10} filter samples collected over the year 2010–2011 in Hamme, Belgium. The levoglucosan data were taken from Maenhaut et al. (2012).

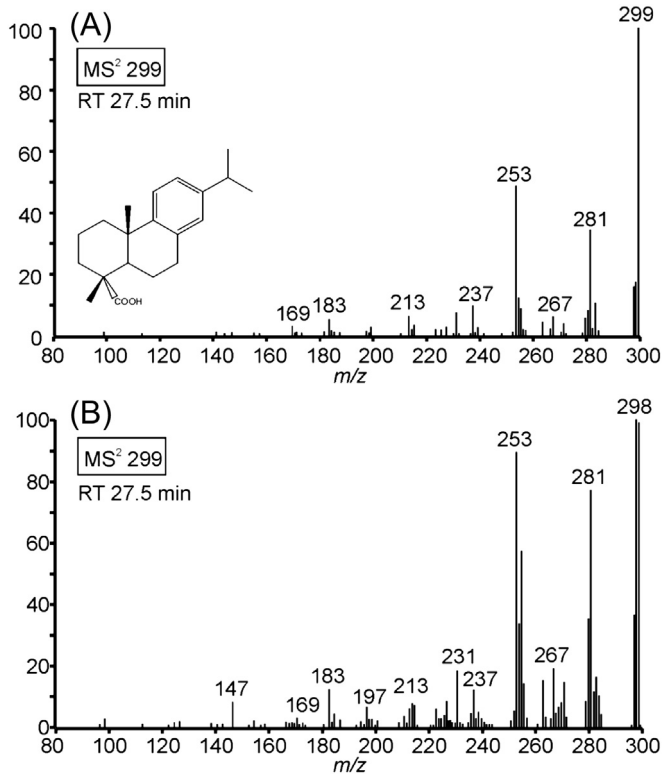

Fig. 4. MS^2 product ion spectra obtained for (A) dehydroabietic acid (standard) and (B) the compound eluting at the same retention time (27.5 min) in an ambient filter sample collected on 2 November 2010 in Hamme, Belgium.

and 10.3%, respectively, $n = 15$) at an urban background location in Ljubljana, Slovenia. The similarity in seasonal variations of the nitro-aromatic compounds and the anhydrosugars together with the good correlations between both types of compounds suggests that wood burning is an important source of the nitro-aromatic compounds. The MW 295 nitrooxy-organosulfates, which are derived from α-pinene, exhibited their highest concentrations in winter, which was a surprising finding. It was suggested that a substantial fraction of these compounds is related to wood burning in winter. DHAA, an indicator for softwood burning, was highly correlated with the anhydrosugars and substantially with the nitro-aromatic compounds, which indicates that the burning of softwood is important at our site. This finding corroborates (at least qualitatively) the study by Maenhaut et al. (2012), who estimated that softwood accounts for 70% of the wood burned at the site.

Wood burning is an important contributor to atmospheric PM_{10} in several European countries, especially in winter, and it may be responsible for a number of exceedances of the EU daily PM_{10} mass limit of 50 μg m^{-3} (Maenhaut et al., 2012). Therefore, it is a target for better emission control in the cold season. On the other hand, EU forecasts anticipate a 57–110% increase in biomass burning between 2000 and 2020 (Wagner et al., 2010). Since the composition of BBA and the wood smoke PM levels depend on the type of wood stove and the type of wood burned, decreasing emissions with improved wood stoves should lead to lower atmospheric levels of potentially toxic nitro-aromatic and other compounds.

Acknowledgments

The samples analyzed for this study were provided by the Flemish Environment Agency (VMM) and were obtained within the Chemkar 3 project. Research at the University of Antwerp was supported by the Belgian Federal Science Policy Office through the network project “Biogenic Influence on Oxidants and Secondary Organic Aerosol: theoretical, laboratory and modeling investigations (BIOSOA)”.

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