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Functional group composition of ambient and source organic aerosols determined by tandem mass spectrometry

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Abstract

The functional group composition of various organic aerosols (OA) is being investigated using a recently developed analytical approach based on atmospheric pressure chemical ionisation-tandem mass spectrometry (APCI-MS/MS). The determinations of the three functional groups' contents are performed quantitatively by neutral loss (carboxylic and carbonyl groups) and precursor ion (nitro groups) scanning modes of a tandem mass spectrometer. Major organic aerosol sources are studied: vehicular emission and wood combustion for primary aerosol sources; and a secondary organic aerosol (SOA) produced through photo-oxidation of o-xylene. The results reveal significant differences in the functional group contents of these source aerosols. The laboratory generated SOA is dominated by carbonyls while carboxylics are preponderate in the wood combustion particles. On the other hand, vehicular emissions are characterised by a strong nitro content. The total amount of the three functional groups accounted for 1.7% (vehicular) to 13.5% (o-xylene photo-oxidation) of the organic carbon. The diagnostic functional group ratios are then used to tentatively differentiate sources of particles collected in an urban background environment located in an Alpine valley (Chamonix, France) during a strong winter pollution event. The three functional groups under study account for a total functionalisation rate of 2.2 to 3.8% of the organic carbon in this ambient aerosol, which is also dominated by carboxylic moieties. In this particular case study of a deep alpine valley during winter, we show that the nitro- and carbonyl-to-carboxylic diagnostic ratios can be a useful tool to distinguish the sources. In these conditions, the total OA concentrations are highly dominated by wood combustion OA. This result is confirmed by an organic markers source apportionment approach which assesses a wood burning organic carbon contribution of about 60%. Finally, examples of functional group mass spectra of all aerosols under study are presented, and additional perspectives offered by the mass spectra in terms of the OA characterisation are discussed.

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1 Introduction

It is now well known that climate and air quality are significantly affected by the composition of the atmospheric organic aerosol (OA) (Kanakidou et al., 2005; IPCC, 2007). However, in spite of the wide range of analytical techniques employed, our knowledge and understanding of the physico-chemistry, formation mechanisms, sources and toxicity of the atmospheric OA are still very incomplete (Fuzzi et al., 2006). The OA is a complex environmental matrix composed of thousands of organic compounds including a significant fraction of high molecular weight compounds (Pio et al., 2001; Graber and Rudich 2006). Its chemical characterisation is generally only achieved, at best, for 20% by mass using molecular analysis techniques, mainly owing to the insufficient resolution and identification capabilities offered by chromatographic systems (Cappiello et al., 2003; Hamilton et al., 2005; Decesari et al., 2006). On the other hand, total carbon analysis and aerosol mass spectrometer analysis (AMS) provide a complete description of the POM, but only limited information relative to the chemical composition (Ruellan and Cachier, 2001; Cao et al., 2005; Lanz et al., 2008). Although huge progresses have been accomplished during the last decade regarding OA chemical characterisation, analytical efforts should be pursued to improve the chemical compositional dataset and reduce the uncertainties related to the organic fraction chemistry of atmospheric aerosol. In particular, functional group analysis appears as a valuable approach in order to better assess the processes involved in new emerging issues regarding OA, such as chemical aging of both primary and secondary OA (Donahue et al., 2009; Hallquist et al., 2009).

The usual analytical technique for functional group analysis is Fourier-Transform InfraRed spectroscopy (FTIR). However, this technique suffers from relatively weak robustness in quantitative determination and difficulties in separating carbonyls from other carboxylics (Blando et al., 2001; Maria et al., 2002). In the past decade, quantitative results were achieved using proton nuclear magnetic resonance ($^1\text{H-NMR}$) for the analysis of the carboxylic and carbonyl functional groups (Decesari et al., 2000; Moretti

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et al., 2008), and using solid-state ^{13}C -NMR for the determination of carboxylic acids (Sannigrahi et al., 2007). The NMR methods still present difficulties for precise signal assignment in complex mixtures as well as high detection limits, especially using ^{13}C -NMR. However, recent applications of ^1H -NMR to the functional group chemical characterisation of atmospheric aerosol samples gave promising results for the study of the secondary organic aerosol (SOA) formation (Moretti et al., 2008) and for source attribution of marine, biomass burning and SOA impacted atmospheric aerosols (Decesari et al., 2007).

Recently, tandem mass spectrometry (MS/MS) was applied to develop quantitative methods for the analysis of carboxylics, carbonyl and nitro functional groups (Dron et al., 2007, 2008a, b). These MS/MS methods combine high sensitivity and good accuracy, and additionally make it possible to obtain an apparent molecular weight profile of the compounds bearing the functional group under study. In the present study, these analytical methods are applied to characterise the carboxylic, carbonyl and nitro content of various aerosols. We studied some major sources of fine organic aerosol, i.e. vehicular exhaust, wood combustion and SOA formed through photo-oxidation of o-xylene under laboratory conditions. On the other hand, we investigated the functionalisation of ambient atmospheric aerosols collected in a suburban site of an alpine valley in winter (Chamonix, France). All of these types of aerosols are compared in terms of molecular weight profiles, functional group distributions, and functionalisation rates. Finally, further interpretations regarding the influence of combustion processes and the use of the results for source apportionment of the atmospheric aerosol are also discussed and evaluated.

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2 Experimental

2.1 Sampling sites and conditions

Samples from various experiments and field campaigns are studied; the sampling conditions and the analyses performed on the sample series are synthesized in Table 1.

2.1.1 Secondary organic aerosols

A series of 4 secondary organic aerosol (SOA) samples were collected during o-xylene photo-oxidation experiments initiated with HONO, in the EUPHORE simulation chamber (European Photoreactor, Valencia – Spain, Becker et al., 1996). Experiment A was carried out at high initial concentration levels in o-xylene and HONO (600 ppb_v o-xylene, 150 ppb_v HONO). Two filters were collected during the whole time of experiment A which lasted for 04:15. Experiment B was carried out at moderate initial concentrations (200 ppb_v o-xylene, 100 ppb_v HONO). Two samples were collected during the whole time of experiment B, which lasted for 05:50. Particles were collected on 47 mm quartz fiber filters (QM-A, Whatman) at a flow rate of 1.5 m³ h⁻¹, downstream a charcoal-impregnated denuder was used to remove the volatile organic compounds (Eatough et al., 1999).

2.1.2 Emission sources aerosols

Aerosols emitted by the combustion of the same sets of wood in 3 different burning devices are studied. The sets of wood were composed of beechwood logs (50 cm long and at least 6 cm large) containing 16% humidity. The wood combustion devices were heating stoves, one recent and one old model, both used for personal heating, and an indoor fireplace. In each case, 47 mm quartz fiber filters (QM-A, Whatman) were collected at reduced and nominal (optimal) combustion efficiencies. These 6 aerosol samples were collected in the chimney outlets on the roofs of residential homes, through a heated rod (125 °C) at a flow rate of 1 m³ h⁻¹ and during 6 h.

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Organic aerosol emitted by road traffic in a roadway tunnel was also considered. A full description of the sampling site and the sample collection procedures is presented in El Haddad et al. (2009). Briefly, the sampling site was located in a French roadway tunnel (Tunnel, Marseilles) where heavy-duty trucks are prohibited and speed is limited to 50 km h⁻¹. PM_{2.5} and PM₁₀ samples were collected on two separate days, on 150 mm quartz fiber filters (QM-A, Whatman) by means of a DA-80 high volume sampler operating at a flow rate of 30 m³ h⁻¹. The final 4 samples assigned to a functional group determination were two separate combinations of 12 PM_{2.5} filters and two separate combinations of 9 PM₁₀ filters, all collected between 07h00 and 08h00, therefore, reflecting whole day emissions in the roadway tunnel, i.e. including both fluid and dense traffic episodes.

2.1.3 Urban background aerosols

Eleven consecutive samples were collected at an urban background site located in the Chamonix Alpine valley (France) from 11–18 December 2007. The sampling site (Clos de l'Ours) is described by Marchand et al. (2004). The Chamonix valley is narrow and surrounded by elevated mountains reaching 3000 to 4800 m above sea level (m a.s.l.) and is characterised by some of the steepest slopes in the Alps. The field campaign was conducted during an atmospheric pollution event characterised by high concentrations in PM₁₀ (avg. 35 µg m⁻³, max. 100 µg m⁻³), NO (avg. 107 ppb, max. 640 ppb) and NO₂ (avg. 71 ppb, max. 177 ppb) associated with low temperatures (avg. -11.2 °C, min. -15.6 °C, max. -3.5 °C) and strong inversion layers.

PM₁₀ were collected on 150 mm quartz fiber filters (QM-A, Whatman) using a DA-80 high volume sampler (30 m³ h⁻¹). The sampling was split into 12 h periods, from 06:00 to 18:00 (UTC) for daytime samples, and from 18:00 to 06:00 (UTC) for nighttime samples. The filters collected during the nights of 11 and 12 December 2007 were put together in order to perform both functional groups and organic tracers analyses on the same filters, as well as 12/12 and 13/12 day filters, 15/12 and 16/12 night filters, and 16/12 and 17/12 day filters. Another set of filters dedicated to OC and EC measure-

ments were collected on Whatman QM-A at a flow rate of $1.5 \text{ m}^3 \text{ h}^{-1}$ on the same time basis as the filters assigned for functional group determination. All filters used in this study were previously fired for 2 h at 500°C to lower the blank levels. All samples were stored at -18°C in aluminium foil sealed in polyethylene bags until analysis.

2.2 Functional group analyses

The functional group analyses were carried out on a triple quadrupole mass spectrometer (Varian 1200L) equipped with an atmospheric pressure chemical ionisation (APCI) source and a high-performance liquid chromatography device (HPLC, Varian Prostar 210). The analytic techniques enable the quantitative determination of the carboxylic, carbonyls and nitro functional groups. They are based on the ability of the functional groups under study to lose a specific neutral molecular fragment (neutral loss scanning) or to produce a characteristic ion (precursor ion scanning) in the collision cell (Dron et al., 2007, 2008a, b). Mass spectra were recorded between m/z 115 and m/z 800, except for the photo-oxidation experiments which were limited in the high masses to m/z 600. Calibration samples were analysed within each sequence. Filter blanks were checked for each functional group determination and the results were all below detection limits.

The filters were extracted using an accelerated solvent extractor (ASE, Dionex) with a solvent mixture of methanol/hexane (2:1, v/v , HPLC-grade from Sigma-Aldrich) and under the following conditions: 100°C and 100 bar during a 5 min static time. The extracts were then evaporated to a volume of 0.5 mL at room temperature and under a gentle stream of nitrogen by means of an automatic concentrator (TurboVap II). The samples were finally dissolved with methanol to a final volume of 3.5 mL.

A $300 \mu\text{L}$ fraction of the extracts was first submitted to the derivatisation of the carboxylic functional groups into their corresponding methyl esters, by adding $300 \mu\text{L}$ of a boron trifluoride methanolic solution ($\text{BF}_3/\text{methanol}$ 14%, v/v , Sigma-Aldrich) and heating it for 2 h at 70°C . The sample was then directly injected, i.e. without chromatography.

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graphic separation, into the APCI chamber at a flow rate of 0.5 mL min^{-1} , and the analysis was performed by recording the total ion current (TIC) measured by scanning the neutral loss of methanol (CH_3OH , 32 amu) from the fragmentation of the protonated methyl esters. In order to avoid any interference or unwanted compounds, a mass spectrum obtained by neutral loss scanning of 32 amu (NL 32) was also recorded before derivatisation, and the corresponding signal was subtracted from the one recorded after derivatisation (Dron et al., 2007).

The determination of the carbonyl functional groups, i.e. aldehyde and ketone groups, was carried out after derivatisation with pentafluorophenylhydrazine (PFPH, Sigma-Aldrich). $150 \mu\text{L}$ of a 0.1 M methanolic solution of PFPH were added to $450 \mu\text{L}$ of the initial sample extract, and the mixture was left to react 18 h at room temperature. The analysis was then performed by directly injecting the solution into the APCI chamber at a flow rate of 0.5 mL min^{-1} , and monitoring the neutral loss of 181 amu (NL 181) from the fragmentation of the protonated hydrazone derivatives. A mass spectrum of the same sample obtained by NL 181 before derivatisation was recorded and subtracted from the spectrum obtained after the PFPH derivatisation (Dron et al., 2008a).

A final fraction of the sample extract was analysed in order to determine the concentration in nitro functional groups. The sample was directly injected in the ionisation source at a flow rate of 0.5 mL min^{-1} , negatively ionised, and the nitro compounds were simply determined by monitoring the precursor ions of the NO_2^- product ion, m/z 46 (PAR 46) (Dron et al., 2008b).

The detection limits of the analytical procedures were 0.005 mM , 0.004 mM , and 0.001 mM for carboxylic acids, carbonyls and nitros, respectively. According to the $30 \text{ m}^3 \text{ h}^{-1}$ flow rate during the 12 h sampling conditions and a sample volume of 3.5 mL , these detection limits correspond to atmospheric concentrations of 0.05 nmol m^{-3} , 0.04 nmol m^{-3} and 0.01 nmol m^{-3} for carboxylic, carbonyl and nitro functional groups, respectively. In terms of OC functionalisation rates, they can be expressed as 0.04% , 0.04% and 0.01% of OC for a sample presenting an OC concentration of $1 \mu\text{g m}^{-3}$. These detection limits are 10 times and 100 times lower than what was reported in

the literature using H-NMR for carboxylic (Tagliavini et al., 2006) and carbonyl moieties (Moretti et al., 2008), respectively. Quantitative functional group analyses of nitro compounds has not been reported in OA since Gordon et al. (1988) and was only performed using FT-IR until the development of our quantitative MS/MS method (Dron et al., 2008b). In the present study, OC concentrations ranged in Chamonix from 9 to 34 $\mu\text{g m}^{-3}$ (Table 2) leading to actual detection limits below 0.001% in terms of functionalisation rates in this case.

2.3 Organic tracers

Four composite samples, representative of 4 days among the 6 days of the sampling period in Chamonix, were solvents extracted and analysed by gas chromatography-mass spectrometry (GC-MS, Thermo Trace GC 2000 coupled to a Polaris Q ion trap mass spectrometer), following the recommendation of the Desert Research Institute for the analysis of semi-volatile organic compounds (DRI, 2003). Before extraction, samples were spiked with known amounts of isotope-labelled standards, tetracosane-d50 and cholesterol-d6. They were extracted by ASE with a dichloromethane/acetone mixture (1:1, v/v) using the same temperature and pressure conditions as previously. One fraction was directly injected for the quantification of the hopanes and steranes. A second fraction (50 μL) was derivatised before the GC/MS analysis with 50 μL of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, Sigma-Aldrich) containing 10% trimethylchlorosilane (TMCS) in order to convert the organic acids and alcohols into their trimethylsilyl esters and ethers, respectively. The two fractions were analysed using the same GC-MS conditions, i.e. electron impact ionisation at 70 eV and chromatographic separation on a TR-5MS capillary column (ThermoElectron). The quantification of the organic compounds was performed using authentic standards, and the compounds for which no authentic standard was available were quantified using the response factor of compounds with analogous chemical structures (for a detailed list of the standards, see Table 4, Sect. 3.3). Field blank filters were treated with the same procedure. The overall procedure is further detailed in (El Haddad et al., 2009).

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2.4 OC/EC

Samples collected at Chamonix and in the roadway tunnel were analysed for EC and OC using the Thermo-Optical Transmission (TOT) method with a Sunset Lab analyser. The newly developed EUSAAR2 temperature program proposed by Cavalli et al. (2010) was used. The EUSAAR2 method includes temperatures of up to 570 °C for the analysis of OC in 100% He, and up to 870 °C for the analysis of EC in 98% He+2% O₂.

3 Results and discussion

The quantitative results of the 3 functional groups measurements are presented in Table 2, as molar concentrations and functionalisation rates for all the samples under study. The carboxylic, carbonyl and nitro functionalisation rates are also reported in Fig. 1. The functionalisation rates, expressed in % of OC, are calculated using Eq. (1),

$$\text{Functionalisation rate(\%)} = ([\text{functional group}]/[\text{OC}]) \times 100 \quad (1)$$

where [functional group] is the molar concentration of the concerned functional group and [OC] the molar concentration of OC in the aerosol, both expressed in mol m⁻³. Figure 1 shows that the relative contributions of the three functional groups are significantly different from one aerosol source to another.

3.1 Functional groups fingerprints of aerosol sources

The primary vehicular exhaust particles collected in the tunnel are characterised by a low functionalisation rate ranging from 1.7 to 2.2% of OC (Table 2). As a result, only one atom of carbon out of 49 on average bears one of the functional groups under study. In more detail, vehicular exhaust OA presents an important nitro content (0.5 to 1.1%) which equals the carboxylic functionalisation rate (0.6 to 1%). The carbonyl

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functionalisation rate is twice lower, ranging from 0.3 to 0.5% (Table 2). Compared to the other samples, the large nitro content may be linked to the high temperatures of the combustion processes occurring in the vehicle engines (Matthews, 1980; Eberhardt et al., 2003) and can be partially attributed to nitro-PAHs, previously identified in diesel exhaust OA (Heeb et al., 2008). The low content in functional groups containing oxygen atoms (carbonyl and carboxylic acid) is also consistent with the moderate water soluble organic carbon (WSOC) fraction measured, which accounts for 20% of the OC measured inside the tunnel (El Haddad et al., 2009) and with the hydrophobic properties of fresh vehicular exhaust soot particles previously described in the literature (Weingartner et al., 1997).

In contrast, wood combustion particles are characterised by high carboxylic and carbonyl concentrations which can reach $12 \mu\text{mol m}^{-3}$ and $3.5 \mu\text{mol m}^{-3}$, respectively (Table 1). These concentrations are 2 to 3 orders of magnitude larger than those measured inside the tunnel, highlighting the large emissions of organic matter produced by wood combustion compared to vehicular exhaust (Schauer et al., 1999, 2001, 2002). It also shows the significant fraction of highly polar organic compounds (essentially lignin pyrolysis products for the carboxylic and carbonyl moieties, Nolte et al., 2001) and humic-like substances (Graber and Rudich, 2006) associated with these emissions. An important variability of the functional groups concentrations is also observed according to the combustion conditions. As no OC data were available for wood smoke samples, this variability should be observed through the carbonyl-to-carboxylic and nitro-to-carboxylic ratios (Table 3). Nitro functional groups are not detected in the particles emitted by wood combustion in open fire, for both combustion efficiencies, while the particles formed in the heating stoves (old and recent) present nitro-to-carboxylic ratios between 0.01 and 0.1. For comparison purposes, this ratio is close to 1 for the tunnel aerosol (Table 3). This result confirms the influence of the combustion processes on the nitro functional group contents since open fires present the lowest combustion temperature while vehicular emissions are issued from high temperature fuel combustion processes. However, no clear trend is observed between nominal and reduced

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operating conditions for nitro-to-carboxylic ratios in the cases of heating stoves. The carbonyl-to-carboxylic ratio presents relevant characteristics as well. In the wood combustion samples, it is systematically and significantly higher for nominal combustion efficiencies than for reduced combustion conditions. In addition, at high efficiencies, the ratios are significantly lower for open fire emissions than in the heating stoves. Finally, the highest $[R-CO-R']/[R-COOH]$ ratio is observed for the roadway traffic emissions. Consequently, increasing the combustion efficiency would possibly favour the production of nitros and carbonyls compared to carboxylic acids. This confirms that primary combustion aerosols may be characterised by their functional group contents according to the combustion process involved.

SOA formed through photo-oxidation of *o*-xylene exhibit a very different functional group fingerprint. For these experiments, OC is deduced from PM concentrations assuming that PM is only made up of organic matter (OM). On the basis of the structure of the main compounds detected in similar photo-oxidation experiments (Forstner et al., 1997; Aiken et al., 2008), a ratio $OM/OC=1.75$ is used in this study to estimate the OC concentrations. Whereas the functional groups molar concentrations reported in Table 2 are very dependent upon the initial concentrations in *o*-xylene and HONO, the functionalisation rates are similar for the 2 experimental conditions under study. This shows that the initial concentrations in *o*-xylene and HONO has no significant influence on the functionalisation of the SOA formed, at least in the range of concentrations covered in this study. The total functionalisation rates of the *o*-xylene photo-oxidation SOA are particularly high, with approximately 1/9 OC atoms in experiment A and 1/11 OC atoms in experiment B functionalised by carboxylic, carbonyl or nitro groups. The SOA samples are strongly dominated by carbonyl groups (Fig. 1), which represent about 75% of all the functional groups determined here. This result is in good agreement with gas phase photo-oxidation chemistry of VOC/NO_x systems (Camredon et al., 2007). These characteristics are very specific to SOA compared to the two types of primary aerosol observed in our study.

3.2 Chamonix urban background aerosol

The total functionalisation rates, considering the three functional groups under study, range from 2 to 4% for the particles collected in Chamonix (Table 2). All the samples are dominated by carboxylic moieties, with carbonyls and nitros being 2 to 5 times less concentrated (Fig. 2). Moretti et al. (2008) measured by H-NMR similar molar concentrations in urban background aerosols collected in Bologna (Italy) in the May–June period. They reported total carboxylic concentrations ranging from 5 to 50 nmol m⁻³ and total carbonyl concentrations from 4 to 35 nmol m⁻³. The corresponding functionalisation rates were from 6 to 20% and from <3 to 11% of water soluble organic carbon (WSOC) for carboxylic acids and carbonyls, respectively. This is higher than what is measured in the present study, but it shall be noted that WSOC is a very variable fraction of OC, generally representing 30 to 80% of OC and, in addition, includes most exclusively the oxygenated fraction of OC (Decesari et al., 2006; Duarte et al., 2007; Salma et al., 2007). The differences may also result from the sampling period and location especially considering the singularity of the valley of Chamonix during winter characterised by high primary emissions from both road traffic and residential heating (Marchand et al., 2004) associated to unfavourable conditions for SOA formation and chemical aging due to low temperatures (−3.5 to −15.6 °C), low solar irradiance and a lack of long range transport of the aerosol. The relatively low carbonyl content in Chamonix OA compared to the high carbonyl functionalisation rates measured for the photo-oxidation experiments (6 to 11%) supports the assumption that the Chamonix winter OA is mainly of primary origin. Another recent study (Liu et al., 2009) carried out in the area of Mexico City and using FTIR reported functionalisation rates of 5 to 30% for carboxylic acids and 0 to 1% for carbonyls, pointing out that a significant difference can be observed from one sampling site to another.

Moreover, significant variations are observed during the sampling period for the carboxylic and carbonyl concentrations, with ranges from 14.7 to 54.7 nmol m⁻³ and from 4.2 to 10.8 nmol m⁻³, respectively. These variations are linearly correlated with OC

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concentrations, and the correlation coefficients are $R^2=0.84$ and $R^2=0.79$ ($n=11$), respectively. These observations are illustrated in Fig. 2, representing the evolution of the atmospheric concentrations for the three functional groups, together with the OC concentration during the whole sampling period. This result implies that the carboxylic acid and the carbonyl functionalisation rates are fairly constant during the sampling period and that no significant differences are observed between day and night samples. Therefore, we can assume that the sources of the aerosol are homogeneous over the measurement period and that the photo-oxidation processes do not significantly change the composition of the organic fraction of the aerosol in the conditions encountered during the sampling campaign. The carboxylic and carbonyl concentrations measured here are then principally subjected to the evolution of OC concentrations. To a lesser extent, these correlations highlight the reliability of the functional groups analytical procedures newly developed.

The nitro functional group is the least represented in the Chamonix aerosols and the concentrations are relatively stable, ranging from 1.2 to 2.4 nmol m⁻³. Such stability induces a lack of linear correlation with the OC content. In these conditions, the functionalisation rate for nitro groups also presents significant variations during the sampling period, ranging from 0.07 to 0.23%. Although a fraction of the nitro compounds may be formed through radical-initiated reactions of organic compounds (Reisen and Arey, 2005), no correlation between NO_x and nitro functionalisation rates is further observed. This suggests a primary origin of the nitro compounds measured in this study.

3.3 Sources discrimination using functional group fingerprints

As discussed above, the functionalisation rates for carboxylic acids, carbonyl and nitro functional groups reveal strong differences according to the nature of the aerosol source. Therefore, it is interesting to test the ability of these functional groups' fingerprints to discriminate sources of ambient organic aerosol. Samples from a narrow Alpine valley during winter appear as an interesting case study since chemical age-

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ing can be neglected as a first approximation. In addition, vehicular emissions and wood combustion can be considered as the two principal primary sources of urban background aerosol in winter (Schauer and Cass, 2000; Zheng et al., 2002) and in an Alpine valley (Marchand et al., 2004; Sandradewi et al., 2008). The photo-oxidation of o-xylene appears as well as a fair approximation for SOA formation in such conditions (high NO_x concentrations: 178.4 ppb in average, low O_3 concentrations: 3.2 ppb in average, and low biogenic activity, as measured during our sampling campaign) (Finlayson-Pitts and Pitts 2000; Atkinson and Arey, 2003). The functional groups' fingerprints of the 3 sources under study and of the urban background aerosol collected in Chamonix, in winter 2007, can be visualised altogether according to their carbonyl-to-carboxylic and nitro-to-carboxylic functional group ratios, as presented in Fig. 3.

The functional group ratios of the 3 aerosol sources are clearly separated, forming a triangle (points are connected by plain lines in Fig. 3) in which the point corresponding to the Chamonix functional group fingerprint is included. Assuming that the functional groups fingerprints of the three sources described in this study are representative of the emissions and aerosol formation processes inside the Chamonix valley, and that no heterogeneous chemical process has significantly modified the composition of the organic fraction during the aerosol atmospheric residence time, a large contribution of wood burning to the ambient OA can be assessed. This is in agreement with the wide use of wood combustion in the valley and with previous results at the same location (Marchand et al., 2004; Jaffrezo et al., 2005; Aymoz et al., 2007). The predominance of the wood combustion contribution in such environments is also in good agreement with the sources apportionment studies performed by Sandradewi et al. (2008), which attributed 88% of OA to wood burning emissions and by Favez et al. (2009) in similar Alpine valleys during winter. The contribution of vehicular exhaust emissions to OC appears very low in comparison to wood combustion. Finally, regarding the functional groups ratio-to-ratio plot, the SOA contribution appears negligible. This observation is in agreement with recent studies estimating the contribution of SOA may drop below 10% of the total OC in wintertime in US locations (Shivastrava et al., 2007;

Lewandowski et al., 2008).

The results, obtained in the present study, must still be taken with care, due to the hypothesis that the 3 aerosol sources considered must represent all the major sources of the OC in the Chamonix valley. The chemical profile of the vehicular emissions can differ between the Chamonix and the Marseilles tunnel traffic, as the wood combustion emissions may be affected by the wood nature (Schauer et al., 2001; Oros and Simoneit, 2001; Fine et al., 2002) and the combustion processes (Table 2). Finally, considering *o*-xylene photo-oxidation in the presence of NO_x as representative of the total urban background SOA in terms of functional group distributions cannot be assessed, as it is the first quantitative functional group determination of SOA produced in simulation chamber. However, photo-oxidation in the presence of NO_x is considered as the principal source of SOA (Kleindienst et al., 2007).

In order to assess the relevance of functional groups ratios as a diagnostic tool to distinguish sources, a source apportionment approach using organic markers has been performed. Table 4 reports the average concentrations of the selected organic markers quantified in the Chamonix aerosol during the same sampling campaign, including hopanes and steranes emitted by vehicular emissions and different wood combustion markers such as levoglucosan, retene, sterols, and guaiacyl and syringyl derivatives. The contributions of these two major sources (OC_{source}, expressed in μg m⁻³) can be calculated following Eq. (2),

$$OC_{\text{source}} = [M]/([M]/OC)_{\text{source}} \quad (2)$$

where [M] is the concentration of a source-specific marker determined in the ambient samples (expressed in ng m⁻³) and ([M]/OC)_{source} is the fractional abundance of the considered organic marker to OC in the source aerosol (expressed in mg g⁻¹).

Because of its ubiquity in all wood combustion aerosols, the levoglucosan is widely used for estimating the amount of OC from wood or biomass combustions in the ambient aerosol. The (levoglucosan/OC)_{wood} ratio, determined by Fine et al. (2002), is quite variable according to burning conditions and wood types. Typically, a ratio of

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42 mg g⁻¹ is found for softwood combustions, while a higher ratio of 136 mg g⁻¹ is found for hardwood combustions. The wood type used predominantly for the combustion can be determined using the other wood combustion markers. The syringyl derivatives and β -sitosterol are found, to a much greater extent, in the hardwood smokes. Accordingly, a $(\beta\text{-sitosterol/OC})_{\text{wood}}$ ratio of 2.9 mg g⁻¹ is reported for hardwood combustions, while a much lower ratio of 0.2 mg g⁻¹ is reported for softwood combustions (Fine et al., 2002). In contrast, retene is an alteration product of the resin acids found in conifers (softwood), and is exclusively emitted from softwood combustions ($(\text{retene/OC})_{\text{softwood}}=5.1 \text{ mg g}^{-1}$) (Fine et al., 2002). The high concentrations of syringyl derivatives and β -sitosterol ($\beta\text{-sitosterol/OC}=2.3 \text{ mg g}^{-1}$) and the low concentration of retene ($\text{retene/OC}=0.33 \text{ mg g}^{-1}$) found in the samples from Chamonix suggest that the aerosol is mainly produced by hardwood combustion. The results presented for functional groups' determinations, performed considering beechwood (hardwood) combustion in various heating devices are, thus, well suited to estimate the wood combustion contribution in the Chamonix valley. Considering the average (levoglucosan/OC) ratio, the mean wood combustion contribution is estimated to 61% of OC ($\text{OC}_{\text{wood}}=9.9 \mu\text{g m}^{-3}$). Comparable contributions of wood combustions to OC concentrations (50–80%) are found in winter using the same methodology, at background sites in Europe (Puxbaum et al., 2007; Favez et al., 2009). These results confirm the prominence of wood combustion in the Chamonix aerosol.

The contribution of the vehicular emissions to OC is calculated using Eq. (2) and hopane as a specific marker of vehicular emissions (Rogge et al., 1993). The same tunnel samples were used for functional groups analyses and for the determination of the $(\text{hopane/OC})_{\text{road}}$ ratio of 0.206 mg g⁻¹ used here (El Haddad et al., 2009). The average contribution of the vehicular emissions to the OC is estimated to 14% ($\text{OC}_{\text{vehicles}}=2.27 \mu\text{g m}^{-3}$). The remaining OC (20.2%) is attributed to the SOA contribution along with other minor primary sources.

The functional groups' diagnostic ratios approach gives rather consistent results compared to the organic markers approach. Nevertheless, these encouraging results

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obtained in source apportionment by MS/MS functional group analysis must be confirmed and supported by the study of additional aerosol sources and by longer atmospheric measurement series in various environments, especially during summer. Chemical aging of the aerosol must also be investigated in terms of modifications in the functionalisation rates. Recent studies have shown a rapid and significant evolution of the organic fraction of primary aerosol (wood combustion and diesel emissions) due to photo-oxidation processes (Sage et al., 2008; Grieshop et al., 2009; Favez et al., 2009). These chemical modifications can greatly affect the functional group distribution and, thus, the ability of functional groups to distinguish the aerosol sources.

3.4 Apparent mass distributions of functional groups

The mass spectra recorded are an additional source of information offered by APCI-MS/MS functional group analysis. They provide a visualisation of the apparent mass distribution of all the detected ions bearing the functional group under study. Examples of mass spectra recorded in the NL 32 mode for the quantification of total carboxylic acids for each aerosol category are presented in Fig. 4. Their global aspects are quite similar, and the average molecular weights of the detected compounds are around m/z 200 for the SOA and vehicular exhaust particles, and around m/z 260 for the wood combustion and Chamonix aerosols. A 15 amu subtraction is necessary in obtaining the carboxylic molecular weight from the corresponding methyl ester derivatives. These results are particularly close from the 248 g mol^{-1} average molecular weight calculated by a thermodynamic method recently applied to a biomass burning aerosol (Asa-Awuku et al., 2008). Ions are detected at nearly every m/z ratios in the vehicular exhaust, wood combustion and urban background aerosols (Fig. 4), attesting to the extreme chemical complexity of OA. All of the aerosols studied here also present a large fraction of peaks above m/z 300, which could characterise a large HULIS content (Dron, 2008).

This is consistent with the large unresolved fraction classically found in atmospheric OA often attributed to this type of compound, constituting up to 30% of the total OC in ambient air (Hamilton et al., 2005; Feczko et al., 2007; Salma et al., 2007). Also, recent

studies proposed wood combustion as a major source of HULIS (Lukacs et al., 2007; Asa-Awuku et al., 2008; Baduel et al., 2009). The samples from wood combustion and from Chamonix urban background contain the largest amounts of high molecular weight compounds, which is consistent with the results indicating wood combustion primary particles as the main component of the aerosol in the Chamonix Valley.

As for carboxylic acids, the mass spectra recorded for the determination of carbonyls and nitros are relatively similar in terms of apparent mass distributions whatever the sample. Carbonyls are also detected up to m/z 500, but nitro functional groups are not detected above m/z 300. This indicates that the high molecular weight compounds encountered in atmospheric OA such as HULIS contain significant amounts of carboxylic and carbonyl groups. They do not present detectable levels of nitro functional groups, as reported by other studies pointing out that HULIS are mainly composed of oxygenated functional groups (Havers et al., 1998; Reinhardt et al., 2007) together with organosulfates and organonitrates (Reemtsma et al., 2006).

4 Conclusions

The MS/MS functional group analysis was applied to the characterisation of the OA from primary and secondary sources, and from an ambient aerosol. The detection limits and the good quantitative accuracy offered by the new MS/MS functional group analytical methods make them a powerful and complementary tool for the characterisation of the OA. In the present study, the carboxylic, carbonyl and nitro functional groups could be detected at the nmol m^{-3} level. Carboxylics represented about 2.0% of the organic carbon in the SOA and ambient samples, but only 0.8% in the vehicular emissions OA. The aerosol sources showed characteristic functional groups distributions, in particular with a high carbonyl content in the o-xylene laboratory generated SOA (6 to 11% of OC) and a high nitro content in the vehicular emissions (0.8% of OC). These specificities enabled the establishment of diagnostic functional group ratios. Then the source contributions of an ambient aerosol was evaluated and showed

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a good agreement with an organic tracer approach performed on the same samples.

The results presented here offer interesting perspectives in OA characterisation. The MS/MS functional group analysis methods are theoretically applicable to all chemical functional groups. For instance, the additional determination hydroxyl, organonitrates and organosulfates groups would provide very valuable compositional data and knowledge relative to the aerosol chemistry. Aerosol aging may also be investigated through the systematic measurement of functional groups in different locations and during significant time periods. The study of aerosol sources can also be completed with additional sources to provide a better accuracy in evaluating the source contributions of an ambient aerosol.

In addition to the quantitative results, the MS/MS technique for functional group determination provides a second type of information through the recorded mass spectra. For instance, the molecular weight distribution of the detected compounds may reveal qualitatively the content of humic-like substances inside the sample under study.

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Table 1. Overview of the samples under study: analyses performed, sampling conditions and number of filters collected (*N*) for each series.

Samples and analyses	Sampling conditions	Filter collection	<i>N</i>
Urban background			
Functional group	Chamonix, December 2007	PM ₁₀ , 12 h at 30 m ³ h ⁻¹	11
Organic speciation		PM ₁₀ , 12 h at 30 m ³ h ⁻¹	4
OC/EC		PM ₁₀ , 12 h at 1.5 m ³ h ⁻¹	11
Vehicular emissions			
Functional group, OC/EC	Marseille (tunnel)	PM _{2.5} , 1 h at 30 m ³ h ⁻¹	2 ^a
		PM ₁₀ , 0.5 h at 30 m ³ h ⁻¹	2 ^a
Wood combustion			
Functional group	old heating stove	PM ₁₀ , 6 h at 1 m ³ h ⁻¹	2
	recent heating stove	PM ₁₀ , 6 h at 1 m ³ h ⁻¹	2
	indoor fireplace	PM ₁₀ , 6 h at 1 m ³ h ⁻¹	2
Photooxidation experiment A			
Functional group, OC/EC	EUPHORE xylene=600 ppb HONO=150 ppb	PM _{2.5} , 04:15 at 1.5 m ³ h ⁻¹	2
Photooxidation experiment B			
Functional group, OC/EC	EUPHORE xylene=200 ppb HONO=100 ppb	PM _{2.5} , 05:50 at 1.5 m ³ h ⁻¹	2

^a Composite of 12 different filters for each two PM_{2.5} samples and composite of 9 different filters for each two PM₁₀ samples.

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Table 2. Carboxylic, carbonyl and nitro functional groups molar concentrations (nmol m^{-3}), corresponding functionalisation rates (%) and OC ($\mu\text{g m}^{-3}$) measured in the different types of atmospheric aerosols: urban background, road traffic and wood combustion emission sources, and SOA formation from o-xylene photo-oxidation.

	R-COOH	R-CO-R'	R-NO ₂	OC ($\mu\text{g m}^{-3}$) mean (range)
Urban background, Chamonix				21.0 (9.01–33.9)
molar mean (nmol m^{-3})	36.3	7.57	1.95	
molar range (nmol m^{-3})	14.7–54.7	4.19–10.8	1.19–2.38	
functionalisation mean (%)	2.1	0.5	0.1	
functionalisation range (%)	1.6–3.1	0.3–0.6	0.1–0.2	
Vehicular emissions				54.7 (34.5–68.2)
molar mean (nmol m^{-3})	38.4	15.7	37.1	
molar range (nmol m^{-3})	29.1–55.7	10.7–21.7	27.6–50.2	
functionalisation mean (%)	0.8	0.3	0.8	
functionalisation range (%)	0.6–1.0	0.3–0.5	0.5–1.1	
Wood combustion				no data
molar mean (nmol m^{-3})	4990	853	68.4	
molar range (nmol m^{-3})	505–12540	159–3480	n.d.–183	
functionalisation mean (%)	–	–	–	
functionalisation range (%)	–	–	–	
Photooxidation experiment A				84.0 (54.4–114) ^b
molar mean (nmol m^{-3})	154	521	38.2	
molar range (nmol m^{-3})	133–174	428–612	23.8–52.6	
functionalisation mean (%)	2.0	6.7	0.4	
functionalisation range (%)	2.0–2.0	6.4–7.0	0.3–0.6	
Photooxidation experiment B				15.9 (13.5–18.3) ^b
molar mean (nmol m^{-3})	28.8	115	4.85	
molar range (nmol m^{-3})	28.5–29.1	101–130	4.16–5.53	
functionalisation mean (%)	2.0	8.3	0.3	
functionalisation range (%)	1.7–2.4	5.8–10.7	0.3–0.3	

^a association of PM₁₀ and PM_{2.5} samples (El Haddad et al., 2009).

^b PM ($\mu\text{g m}^{-3}$) measured by TEOM (1400 A, R and P), and converted to OC assuming that the particles were exclusively constituted of organic materials, and that OM/OC=1.75 on the basis of the structure of the main compounds detected in similar photo-oxidation experiments (Forstner et al., 1997; Aiken et al., 2008).

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Table 3. Carbonyl to carboxylic and nitro to carboxylic molar concentrations ratios in different wood combustion devices and in the road traffic emissions collected in the tunnel, Marseille (France).

	R-CO-R'/R-COOH	R-NO ₂ /R-COOH
Wood combustion ^a		
Recent stove, nominal	0.29	0.01
Recent stove, reduced	0.15	0.05
Old stove, nominal	0.32	0.10
Old stove, reduced	0.04	0.01
Open fire, nominal	0.19	n.d.
Open fire, reduced	0.14	n.d.
Tunnel roadway (mean, <i>n</i> =4)	0.41±0.19	0.97±0.49

n.d., R-NO₂ not detected. ^a For each wood combustion experiment, one sample was analysed and the applicable variability is limited to the analytical deviations: 12, 19.5 and 18% for carboxylics, carbonyls and nitros, respectively (Dron et al., 2007, 2008a, b).

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Table 4. Concentrations of organic tracers measured in the filter samples (average values, ng m^{-3}) collected in winter 2007 in Chamonix (France) and calculated contributions of wood combustion and road traffic emission sources (refer to text for the details of the contributions calculations).

Organic compounds mean concentrations [ng m^{-3}]					
compounds	Average concentrations	Note	compounds	Average concentrations	Note
steranes					
5 α (H),14 β (H),17 β (H)-Cholestane	0.28±0.13	b	5 α (H),14 β (H),17 β (H)-Ergostane	0.25±0.10	b
5 α (H),14 α (H),17 α (H)-Cholestane	0.42±0.18	a	5 α (H),14 β (H),17 β (H)-Stigmastane	0.52±0.20	b
hopanes					
Trisnorhopane	0.34±0.19	c	17 α (H)-21 β (H)-22S-Homohopane	0.23±0.07	c
17 α (H)-Trisnorhopane	0.33±0.15	c	17 α (H)-21 β (H)-22R-Homohopane	0.125±0.04	c
17 α (H)-21 β (H)-Norhopane	0.72±0.30	c	17 α (H)-21 β (H)-22S-Bishomohopane	0.15±0.10	c
17 α (H)-21 β (H)-Hopane	0.59±0.18	a, +	17 α (H)-21 β (H)-22R-Bishomohopane	0.07±0.05	c
PAH					
Retene	5.2±1.6	d			
guaiacyls derivatives					
Vanillin	51±27	a	3-Guaiacylpropanol	17±4.8	a
Acetovanillone	11±4.7	a	Vanillic acid	21± 7.6	a
Coniferyl aldehyde	65±19	a			
syringyls derivatives					
Syringaldehyde	150±91	a	3-Syringylpropanol	7±6	f
Acetosyringone	67±23	a	Synapyl aldehyde	61±56	g
Propionyl Syringol	30±9	e	Syringic acid	29±8	h
Syringyl acetone	81±52	e	Homosyringic acid	2.0±1.4	h
sugar anhydrides					
Galactosan	70±24	i	Mannosan	140±50	i
Levoglucozan	1340±430	a, ‡			
sterols					
Cholesterol	3.5±0.35	a	Stigmasterol	3.0±0.21	a
Campesterol	3.1±0.45	j	β -Sitosterol	37±7.5	a
Major mass concentration [$\mu\text{g m}^{-3}$]					
OC*	16±4.9		PM2.5*	31±9.1	
Sources contributions to OC [%]					
Wood combustion	61±14				
Vehicular emissions	14±4				
Other sources**	25±15				

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Table 4. Continued.

Footnotes: (a–i) identification notes: The quantification of the organic compounds is based on the response factors of a – authentic standards, b – 20 R, 5 α (H), 14 α (H), 17 α (H)-cholestane, c – 17 α (H)-21 β (H)-hopane, d – phenanthrene, e – syringaldehyde, f – 3-Guaiacylpropanol, g – Coniferyl aldehyde, h – vanilic acid, i – Levoglucosan and j – average response factor of cholesterol and β -sitosterol. (+ and ‡) sources contribution determination notes: Organic compounds used for the determination of the vehicular emissions contribution (+) and the wood combustion contribution (‡).

* Average OC and PM determined for the composite samples on which the organic speciation analyses was carried on.

** Deduced from wood and road contributions assuming that the total of contributions is 100%.

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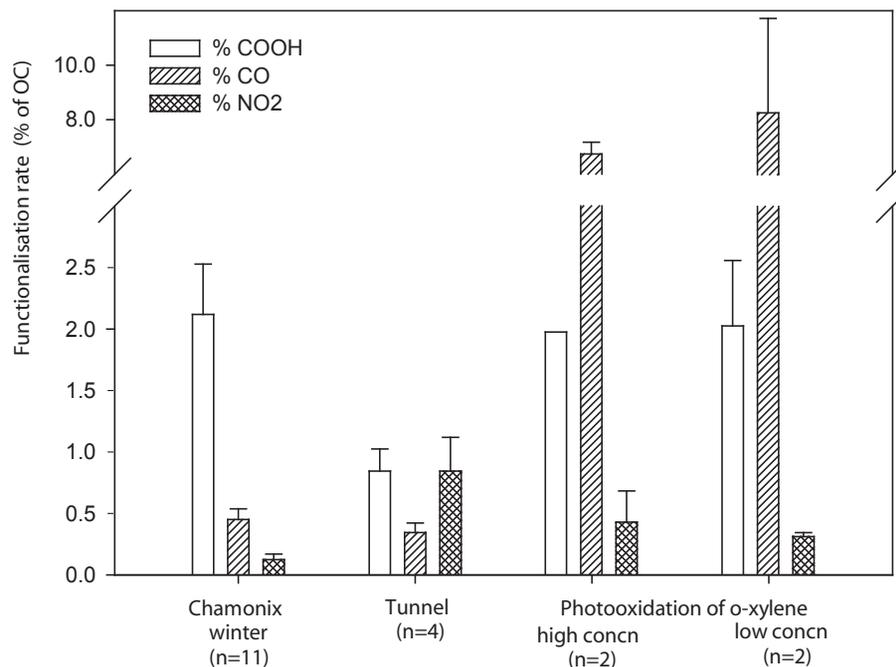


Fig. 1. Functionalisation rates measured in the different aerosols under study. Concentrations are given in terms of functional group molar content normalised to the OC molar content (expressed in% of OC).

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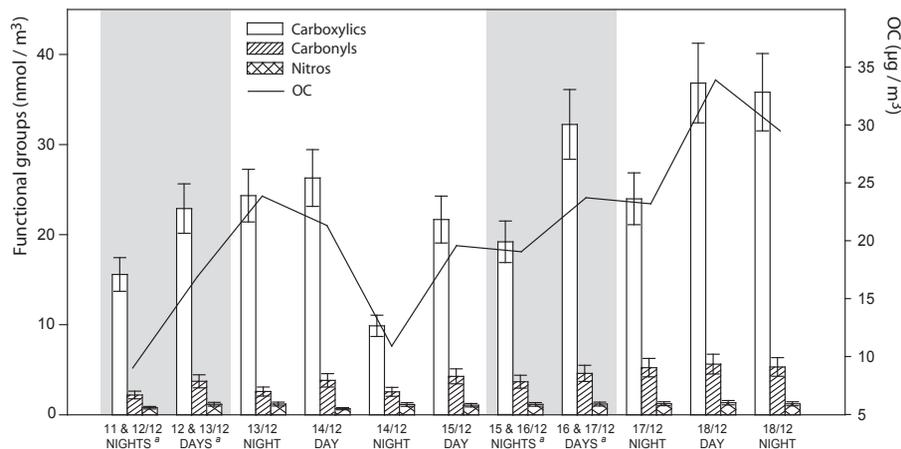


Fig. 2. Carboxylic, carbonyl and nitro functional groups and OC atmospheric concentrations during the Chamonix sampling campaign, in December 2007. The filters were collected following night (18:00 to 06:00 local time) and day periods (06:00 to 18:00 local time). Error bars represent the analytical deviations. The grey backgrounds outline the samples also used for determination of organic tracers. ^aComposite samples of the filters collected at the indicated dates, see text for details (Sect. 2.1.3).

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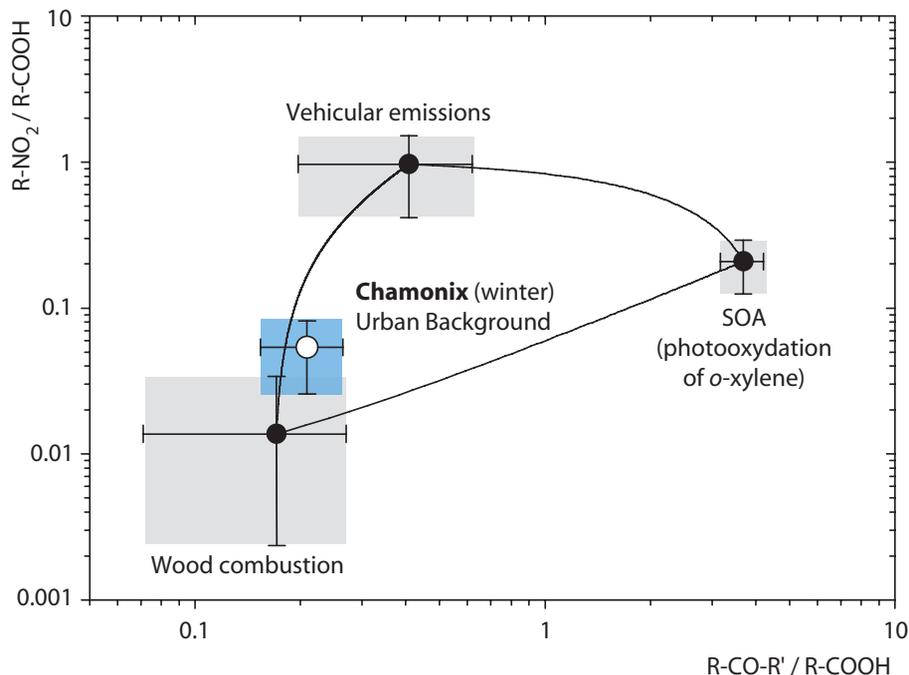


Fig. 3. Average $R\text{-NO}_2/R\text{-COOH}$ and $R\text{-CO-R}'/R\text{-COOH}$ ratios (logarithmic scales) obtained for the 3 aerosol sources (black circles) and for the Chamonix urban background aerosol (white circle). Error bars represent the standard variations calculated for each sample series, $n=6$ for wood combustion, $n=4$ for road traffic, $n=4$ for *o*-xylene photo-oxidation (materialised as grey boxes for the aerosol sources), and $n=11$ for the Chamonix aerosol (materialised as blue box).

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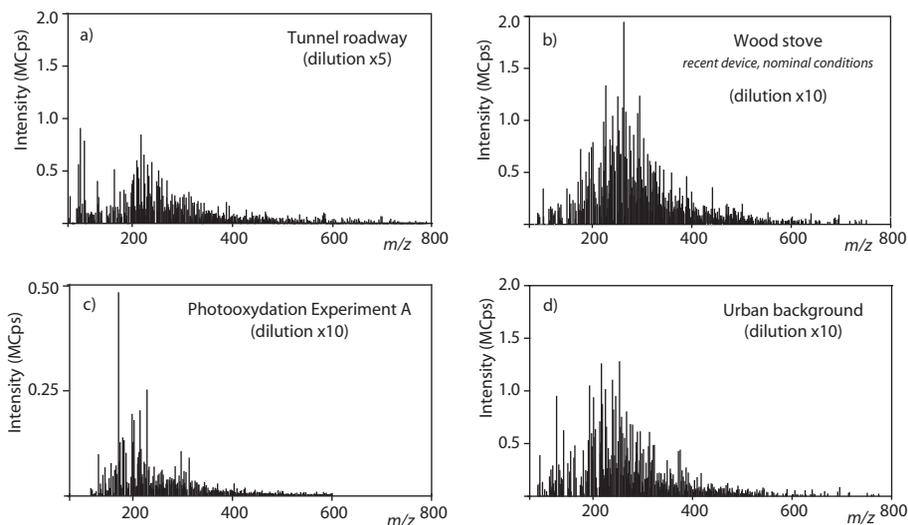


Fig. 4. Carboxylic acids mass spectra recorded by NL32 for **(a)** tunnel roadway, **(b)** wood combustion, **(c)** o-xylene photo-oxidation experiment at high initial concentration levels, and **(d)** urban background samples. As the mass spectra were not recorded during the same sequences, only comparisons based on mass profiles shall be considered, the signal intensities being affected by day-to-day variations.

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