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Aerosolomics based approach to discover source molecular markers: A case study for discriminating residential wood heating vs garden green waste burning emission sources

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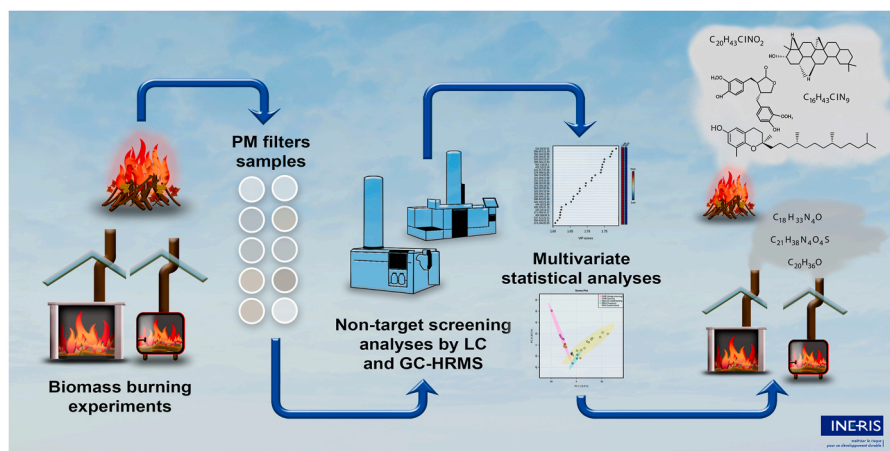
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HIGHLIGHTS

- Fingerprint comparison to reveal markers of green waste burning and wood heating
- Combination of non-target screening characterization with multivariate statistics
- Optimized LC- and GC-HRMS analyses to detect as many species as possible
- 31 markers of green waste burning and 4 of residential wood heating discovered
- Tentative identification of potential molecular formulas of the marker candidates

GRAPHICAL ABSTRACT



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ABSTRACT

Biomass burning is a significant source of particulate matter (PM) in ambient air and its accurate source apportionment is a major concern for air quality. The discrimination between residential wood heating (RWH) and garden green waste burning (GWB) particulate matter (PM) is rarely achieved. The objective of this work was to evaluate the potential of non-targeted screening (NTS) analyses using HRMS (high resolution mass spectrometry) data to reveal discriminating potential molecular markers of both sources. Two residential wood combustion appliances (wood log stove and fireplace) were tested under different output conditions and wood moisture content. GWB experiments were carried out using two burning materials (fallen leaves and hedge trimming). PM samples were characterized using NTS approaches with both LC- and GC-HRMS (liquid and gas

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Non-targeted analysis (NTA)
High-resolution mass spectrometry (HRMS)

chromatography-HRMS). The analytical procedures were optimized to detect as many species as possible. Chemical fingerprints obtained were compared combining several multivariate statistical analyses (PCA, HCA and PLS-DA). Results showed a strong impact of the fuel nature and the combustion quality on the chemical fingerprints. 31 and 4 possible markers were discovered as characteristic of GWB and RWH, respectively. Complementary work was attempted to identify potential molecular formulas of the different potential marker candidates. The combination of HRMS NTS chemical characterization with multivariate statistical analyses shows promise for uncovering organic aerosol fingerprinting and discovering potential PM source markers.

1. Introduction

High-resolution mass spectrometry (HRMS) provides high mass accuracy and resolution to analyze complex environmental mixtures such as organic aerosols (OA) (Krauss et al., 2010; Nizkorodov et al., 2011; Nozière et al., 2015; Schymanski et al., 2014, 2015). The application of non-targeted screening (NTS) strategies using HRMS allowed the detection of thousands of unique chemicals defined as chemical fingerprint. HRMS analyses have been also extensively used for the identification of unknown compounds to better characterize OA according to their origin (Avagyan et al., 2016; Kenseth et al., 2020; Ng et al., 2008; Riva et al., 2016; Röhler et al., 2020, 2021; Surratt et al., 2010; Thoma et al., 2022; Ungeheuer et al., 2021; Vogel et al., 2019; Xu et al., 2021). However, few studies have explicitly exploited the potential of non-targeted HRMS data to identify specific markers or chemical signatures of an emission source. Combining NTS strategies with multivariate statistical analyses (i.e. chemical fingerprint comparison), is useful to highlight specific chemical structures which could be further used in for source apportionment purposes (Peter et al., 2019). Some examples of chemical fingerprint comparison applied to the OA sources showed the relevance of this type of approach in the investigation of specific markers of a given source (Huo et al., 2021; Thoma et al., 2022; Weggler et al., 2016; Yang et al., 2020).

Biomass burning is one of the most important sources of particulate matter (PM) contributing to the air quality degradation. Several studies showed that residential wood heating is a significant contributor to PM concentrations, especially in winter period (Chen et al., 2017, 2022; Denier van der Gon et al., 2015; Fuller et al., 2014; Herich et al., 2014; Kotchenruther, 2016; Olsen et al., 2020; Puxbaum et al., 2007; Srivastava et al., 2018; Viana et al., 2016; Vicente and Alves, 2018; Weber et al., 2019; Zhang et al., 2020). During non-heating periods, biomass burning emissions are related to open-air combustions like wildfires, agricultural open burning and also garden bonfires (Akagi et al., 2011a; Alves et al., 2010b, 2019; Andreae, 2019; Andreae and Merlet, 2001; Crutzen and Andreae, 1990; Hays et al., 2005; Iinuma et al., 2007; Pio et al., 2008; Sommers et al., 2014; Wiedinmyer et al., 2014). Even if banned in several countries, green waste burning (GWB) is a common practice in European countries, especially in sub-urban and rural areas, due to a lack of reliable waste management services, convenience and economic reasons (Cogut, 2017; Eades et al., 2020; Mihai et al., 2019; Wiesen and Ciceu, 2018). These open-air combustions are often associated with large emissions of several particulate toxic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran (PCDD/F), polychlorinated biphenyls (PCBs) (Alves et al., 2019; Andreae, 2019; Hays et al., 2002; Kannan et al., 2005; Kaufmann, 1997; Lutes and Kariher, 1996; Schmidl et al., 2008; Wiedinmyer et al., 2014). Numerous studies pointed out the difficulties and the challenges to precisely apportion the biomass burning sources in ambient air. To our knowledge, the discrimination between residential wood heating (RWH) and GWB aerosols is difficult and rarely achieved. Some authors suggested the use of a gaseous tracer (CH_3Cl) (Edgerton et al., 1984; Khalil et al., 1983) but its application has been limited. Moreover, although this gaseous compound is largely emitted by biomass combustion, it is also emitted by other sources such as ocean, industries, or fungal spores (Keene et al., 1999; Li et al., 2017; Lobert et al., 1999; McCulloch et al., 1999) and

therefore does not appear to be sufficiently specific of GWB. Molecular chemical signatures of GWB have also been suggested such as high carbon preference index (CPI) ratio, low levoglucosan/mannosan ratio, low emissions of sinapaldehyde, high emissions of arabitol and sorbitol (Alves et al., 2019; Hays et al., 2005; Noblet et al., 2021; Rogge et al., 1998; Schmidl et al., 2008). However, specificities regarding biomass sources are limited and confusing factors exist with other combustion sources (softwood combustion or fungal spores notably). The lack of an extended OA characterization of various biomass combustion sources limited the discovery of molecular markers able to discriminate these two sources.

The objective of this study was to evaluate the potential of NTS analyses using HRMS data to reveal discriminating molecular markers of GWB and RWH. Samples have been collected from biomass combustion experiments performed in realistic conditions. Aiming at comprehensively describing the diverse chemical species present in biomass burning samples, the sample preparation has been optimized, and liquid- and gas-chromatography HRMS (LC- and GC-HRMS) have been used for the sample analyses (Huo et al., 2021; Moschet et al., 2017, 2018; Rostkowski et al., 2019). Obtained chemical fingerprints have been compared using several multivariate statistical analyses to discover source specific chemical features (including molecular mass or m/z , retention time and abundance) for GWB and RWH. A complementary work has been attempted to identify the highlighted chemical features.

2. Material and methods

2.1. Combustion experiments and sample collection

Combustion experiments and the PM sample collection procedure have been described previously (Noblet et al., 2021) and details are reported in the supplementary material (SM, section 1). Briefly, biomass burning experiments have been performed in simulated real-world conditions in a large combustion chamber facility (1000 m^3) to simulate the ambient air dilution conditions (close field) and account for post-combustion processes (condensation, evaporation/desorption and chemical reactions including oxidation processes) (Nalin et al., 2016; Nussbaumer, 2008). For GWB, different green waste batches were burnt on a sand-bed located at the center of the combustion chamber. A typical batch included hedge trimming, with branches and leaves (mix of local species including cedar, bay leaf, privet ...) and fallen tree leaves. Additional open-air wood log burning experiments were performed to evaluate the impact of the combustion quality on the chemical fingerprint. RWH experiments were performed using a fireplace and a cast-iron residential wood stove (RWS) under two output conditions (nominal and reduced). For all wood log burning experiments, a mix of beech, hornbeam and oak, the most used wood species for heating purposes in France, has been burnt. Two wood log moistures have been tested (15 and 25%) to evaluate the impact of the humidity on the molecular chemical composition. Simultaneous combustion experiments, RWS together with GWB, have been also performed. All experiments have been carried out at least in triplicates. Overall, 45 p.m. samples and 11 field blanks have been collected on pre-fired quartz fiber filters with a high-volume sampler (Digitel DA-80, $30\text{ m}^3\text{ h}^{-1}$, no size cut) after dilution with ambient air (dilution factor about 500–1000). Modified combustion efficiency (MCE) usually used to characterize the

relative amount of flaming and smoldering combustion (Akagi et al., 2011b; Urbanski, 2013; Yokelson et al., 1996) has been calculated and reflected here the overall combustion performance (see SM for details). Table S1 summarizes the different tested combustion conditions. After collection, samples were wrapped in aluminum foil, sealed in polyethylene bags, and stored at -18°C until analysis.

2.2. Chemical analyses

Details of solvents and chemicals used for the extraction procedures (purity and suppliers) can be found in Table S2. Additional extraction and analytical details, together with quality assurance and control (QA/QC), of the NTS protocol are provided in sections 2 to 4 of the SM. Total carbon (TC) measurements were done by thermo-optical method using a Sunset Lab analyzer following the EUSAAR-2 protocol (Cavalli et al., 2010).

2.2.1. Sample extraction

Prior to extraction, filter samples were spiked with labelled internal standards, named extraction internal standard (EIS) (Tables S3 and S4). These labelled compounds were chosen to be as much as possible representative of species emitted by biomass burning, distributed all over the chromatogram of analysis and regarding their commercial availability and cost. Finally, 5 EIS were selected for LC-ESI-QToF analyses and 8 for the GC-EI-QToF ones (Table S3). The volume spiked on samples has been adjusted according to the final volume of the extract (Table S4). A QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe) procedure has been developed and optimized to perform specific extractions for LC- and GC-HRMS analyses (Albinet et al., 2013, 2014, 2019). 4.9 cm² filter punches ($\varnothing = 25$ mm), including laboratory blanks, have been placed in glass centrifuge tubes and extracted with 6 ml of an acetonitrile/water mixture (50:50) or 100% acetonitrile for LC and GC-HRMS analyses, respectively. Then, tubes have been agitated for 5 min with a multi-position vortex (1700 rpm) (Multi-tube Vortex, DVX-2500, VWR) and centrifuged for 7 min at 4500 rpm using a Sigma 3-16 PK centrifuge. A volume of 4 ml of the supernatant have been collected, filtered (Uptidisc PTFE 13 mm, 0.2 μm porosity), and evaporated under a gentle nitrogen stream near to dryness for LC-HRMS analyses and to 200 μL for GC-HRMS analyses. Residues have been dissolved in an acetonitrile/water (50:50) and 100% acetonitrile for LC- and GC-HRMS analyses, respectively. The final volumes have been adapted according to the sample loading and the instrument used for analysis to avoid signal saturation. The final volume was 200 μL for the residential wood stove samples, fireplace samples, field, and lab blanks (for both instrumental analyses), 2 mL (LC-ESI-QToF) and 1 mL (GC-EI-QToF) for GWB leaves and open-air wood log burning samples, 4 mL (LC-ESI-QToF) and 2 mL (GC-EI-QToF) for GWB hedge trimming and simultaneous combustion samples. A quality control sample (QC pool) was prepared for both analytical methods by pooling a volume of 30 μL of each sample extract.

2.2.2. Non-targeted screening chemical analyses

Before analysis, 20 μL of an injection internal standard (IIS) solution (Table S5) have been added to the extracts to evaluate any analytical drift. LC-HRMS analyses have been carried out on a UHPLC 1290 Infinity coupled to a QToF (Quadrupole-Time of Flight) IFunnel 6550 (Agilent) equipped with an electrospray ionization (ESI) source used in positive (ESI(+)) and negative (ESI(-)) modes. Chromatographic separation of the analytes was done using a C18 column (Acquity HSS T3 C18, 2.1 mm \times 100 mm, 1.8 μm , Waters) equipped with a guard column (Acquity UPLC HSS T3 VanGuard 2.1 \times 5 mm, 1.8 μm , Waters) thermostated at 40°C . The injection volume was 5 μL and elution was performed with methanol (mobile phase B) and water with 1 mM acetic acid and 1 mM ammonium acetate (mobile phase A) at a flow rate of 0.4 mL min⁻¹ with the following gradient: 2% B for 2 min, then increased up to 40% B in 9 min, again increased up to 98% B in 20 min and maintained at 98% B for

5 min. The instrumental operating conditions of the LC-QToF are presented in Table S6. The GC-HRMS analyses have been done with a 7890 GC coupled to a 7250 QToF instrument (Agilent). Electron ionization at 70 eV (high-energy ionization, HEI) and 10 eV (low-EI, LEI) has been used with a source temperature of 280°C . Chromatographic separation by GC was performed on a DB-5MS column (equivalent to 5%-phenylmethylpolysiloxane, 30 m \times 250 μm , 0.25 μm , Agilent J&W) equipped with a guard column (VF-5 MS, 10 m \times 0.25 mm, 0.25 μm , Agilent). 1 μL of the extracts was injected in pulsed splitless mode through an ultra-inert low-fritted liner (870 μL , 4 mm I.D., Agilent). All the operating conditions for GC-EI-ToF are presented in Table S7. Examples of Total Ion Chromatograms (TIC) obtained for each analytical condition are presented on Fig. S1.

To ensure the mass accuracy, calibration of both instruments has been performed before each analytical sequence using a solution provided by the manufacturer. This calibration operation was also integrated every two injections throughout the GC-EI-QToF analytical sequence to limit any mass deviation along the sequence (<2 ppm). For LC-ESI-QToF, a reference solution was continuously injected during the run to check the mass drift of the instrument.

2.3. Quality assurance/quality control (QA/QC)

To ensure the reliability of the NTS analyses and the quality of the data generated, several QA/QC steps have been implemented using IIS, EIS and QC pools. According to the NTS guidelines (Broadhurst et al., 2018), samples (including laboratory, field blanks and QA/QC samples) have been analyzed following a randomized sequence: ten QC pools injected at the beginning of the analytical sequence to condition the analytical system and then regularly injected (every 5 samples) throughout the sequence. Study of the EIS and IIS retention times (RT) and m/z in QC pools showed good analytical reproducibility. Low drifts in retention time of EIS and IIS have been observed but within a tolerance of ± 0.2 min for LC-QToF data and ± 0.1 min for GC-QToF data (Fig. S2, S3 and S8). Acceptable deviations of the m/z ratio (<10 ppm) have been observed for the EIS and IIS for GC- and LC-QToF data. Note that smaller deviations for ESI(-) mode have been obtained compared to the ESI(+) mode for LC analyses (Fig. S4, S5 and S9). For all the different analyses, peak shapes, and areas of EIS in the QC pools have also been monitored. The reproducibility and instrumental drift on the analytical responses was evaluated using control charts for three EIS. The logarithm of the peak areas of the three selected EIS has been plotted according to the injection order (Fig. S6, S7 and S8). The mean area \bar{x} and standard deviation σ has been calculated for each EIS of the QC pools and biomass combustion samples. Most values were within the range $\bar{x} \pm 2\sigma$. Values out of the range have been specifically checked but no trend was found. Finally, no data was excluded. Principal Component Analysis (PCA) score plots have been generated from raw LC- and GC-QToF data for combustion and QC pool samples (S11 and S12). QC pools were tightly clustered, and no outlier or time-related trend was observed.

Field blank analyses have been performed in the same way as the combustion samples. Due to limited computer resources, field blanks were not integrated in the final statistical analysis but treated separately. Even if a large variability could be observed for the analysis of the field blanks for the LC-ESI(+)-QToF analyses, a higher number of features have been detected in combustion samples compared to lab and field blanks (Figs. S13 and S14) inducing a low impact on the subsequent data analysis.

2.4. Feature extraction and multivariate statistical analyses

The Recursive Feature Extraction from Profinder software (Agilent v. B.10.00) was used to process the three-dimensional LC raw data (retention time, m/z ratio and abundance) and the bi-dimensional GC raw data (retention time and abundance) into aligned chromatographic

peaks with associated peak abundances. All parameter settings, the number of detected and selected features in the final dataset are presented in Table S8.

Before statistical analysis, missing values were replaced by a non-impacting value (half of the minimum positive value found in the dataset). Feature abundances have been normalized by the TC content, the dilution factors applied on the extracts (section 2.1.3) and, only for the LC-QToF data, by a compensation factor for matrix effects calculated using the signal obtained for the metsulfuron- d_3 EIS. TC normalization was employed instead of OC or PM because, for numerous samples (e.g., hedge trimming), the distinction between EC and OC was not feasible due to filter overloading. Additionally, the potential loss of semi-volatile species between the emission source and close field (after dilution) during the experiments was observed, as previously reported (Noblet et al., 2021). Finally, data have been auto scaled and no data transformation was applied. Multivariate statistical analyses were performed with MetaboAnalyst (Chong et al., 2019; Xia and Wishart, 2011). Non-supervised methods, such as PCA and agglomerative Hierarchical Clustering Analyses (HCA) have been carried out. The classification used for HCA was performed based on the Pearson correlation coefficient using the average linkage method. Supervised methods, like Partial Least Square-Discriminant Analysis (PLS-DA), has been used to highlight the different chemical signatures associated with residential wood-burning samples and green waste burning samples, construct and validate a model for biomass combustion classification. The quality of the model was evaluated by a leave-one-out cross validation (LOOCV) with two parameters: $R^2(Y)$ and $Q^2(Y)$ (goodness-of-fit). The variable importance in projection (VIP) score was used to select potential RWH and GWB markers and criteria were as follows: VIP score ≥ 1.4 for LC-ESI(-)-QToF and VIP score ≥ 1.5 for both LC-ESI(+)-QTOF and GC-EI-QToF. The VIP score was calculated as the weighted sum of the squared correlations between the PLS-DA components and the original variable. Such score measures the feature's importance in the PLS-DA model and summarizes the contribution of each feature in the model. Higher the VIP score was, more important the feature was in the model and so more discriminating between both biomass burning sources, RWH and GWB.

2.5. Tentative structure identification

Proposition of molecular formulas of the selected markers has been performed based on LC-QToF data with the MassHunter software (Agilent). They were estimated from the $[M + H]^+$ or $[M - H]^-$ ions based on the isotope patterns (isotope abundance and spacing) and low mass error limits ($\Delta m/z \leq 10$ ppm). The following constraints were used: $C \leq 50$, $H \leq 100$, $N \leq 10$, $O \leq 20$, $S \leq 5$ and $Cl \leq 5$. In case of multiple assignments, only molecular formulas with a score (empirical score based on score exact mass, isotope spacing and abundance) higher than 90 were considered. Additional targeted MS/MS analyses (collision energy = 20 eV) were performed using the $[M - H]^-$ or $[M + H]^+$ mass of the selected features. Suggested molecular formulas were validated combining MS/MS data and MetFrag (Ruttkies et al., 2016; Wolf et al., 2010) analysis and searched in databases such as PubChem, Mass Bank Europe and North America. For GC-QToF data, features were extracted with the Agilent Unknowns Analysis program (version B.09.00) with peak detection and grouping using the SureMass deconvolution algorithm with the following parameters: RT window size factor = 80 and extraction window $\Delta m/z = -0.3$ AMU (left) and $+0.7$ AMU (right). For each deconvoluted spectra, a forward search (pure weight factor = 0.7) was done with the NIST17 mass spectra library. A match factor was attributed based spectra similarities and retention index agreement. Retention indices were calculated using a solution of C_8 to C_{40} n -alkanes. NIST17 identifications obtained were manually reviewed. LEI analyses were also performed to identify the molecular peaks (Mairinger et al., 2019). When available, analytical standards were injected to confirm the identity of the substances. A confidence level has been attributed to

each potential identification according to Schymanski's classification (Schymanski et al., 2014).

3. Results and discussion

3.1. Optimization of the analytical procedure

The non-targeted analysis protocol was developed and optimized to get the most comprehensive chemical fingerprints in terms of number of entities extracted and detected, and to reflect as much as possible the sample content. Such developments have been made according to several parameters including the extraction procedure, the solvent of extraction, the sample extract evaporation and dilution. The results obtained are detailed in the SM (section 6, Figs. S15–S20, Tables S9 and S10).

3.2. RWH and GWB chemical signature comparison

PCA were performed to compare the chemical signatures obtained between all biomass burning sample types (Fig. 1). Results showed a good separation along the first PCA component (PC1) between GWB samples and the other wood log combustion conditions tested. All GWB samples, fallen leaves and hedge trimming, were spatially close to each other, except for one sample (848) of hedge trimming, which showed a lower TC value compared to the three other hedge trimming samples. The RWH group, which gathers all the tested conditions for the RWS, formed an extended group, especially for LC-ESI(+)-QToF data. Fireplace samples were observed close to the RWS samples. Complementary PCA including only dry (15%) and humid (25%) wood RWS samples did not display any impact of the wood moisture on the chemical signatures obtained (Fig. S21). Samples from the nominal (822, 823, 825, 840, 861, 862, 863 and 864, MCE = 0.959–0.964) and reduced (826, 827, 828, 829, 839, 865, 866, 867 and 868, MCE = 0.941–0.946) outputs were slightly separated according to PC1. This highlighted that the combustion performances (based on MCE) have larger impact on the chemical signatures than the wood moisture. It is well known, that the combustion conditions play a key role in the chemical composition of the emissions since many species are predominantly emitted during either flaming or smoldering combustion correlating with MCE (Burling et al., 2011; Christian et al., 2003; McMeeking et al., 2009; Urbanski, 2013). Comparing all biomass burning samples (Fig. 1), most of the RWS and fireplace samples contributed positively to PC1 (Fig. 1), while all the GWB contributed negatively to PC1. No clear distribution of the samples, over PC1 or PC2, according to combustion performances (large span of MCE from 0.824 to 0.954, Table S1) was observed whatever the analytical method considered. If within the RWH, the lower combustion performance samples (RWS in reduced output and fireplace, MCE = 0.938–0.956) showed a lower positive contribution to PC1 (close to 0) than the higher performance ones (RWS in nominal output, MCE = 0.59–0.964) (as also shown before on Fig. S21), the distribution of both type of GWB samples (falling leaves and hedge trimming) did not follow the same pattern with MCE of 0.824 and 0.906, respectively. Open-air wood log burning samples (MCE = 0.927) were closer of the RWS and fireplace samples (especially fireplace samples with a similar MCE of 0.938) than the GWB ones. All these results suggested that the chemical signature might be impacted by the combustion performances, but the nature of the fuel was a key parameter in the different chemical fingerprints observed between RWH and GWB.

Two main groups have been formed for further statistical analyses, namely RWH (all RWS and fireplace samples) and GWB (hedge trimming and leaves). Open-air wood log burning was not included in the next analyses, as this condition does not represent a realistic practice (except campfires).

Sample classification data analysis confirmed the PCA results and showed three main sub-groups namely, GWB, RWH with lower combustion performance samples (RWS reduced output and fireplace, MCE

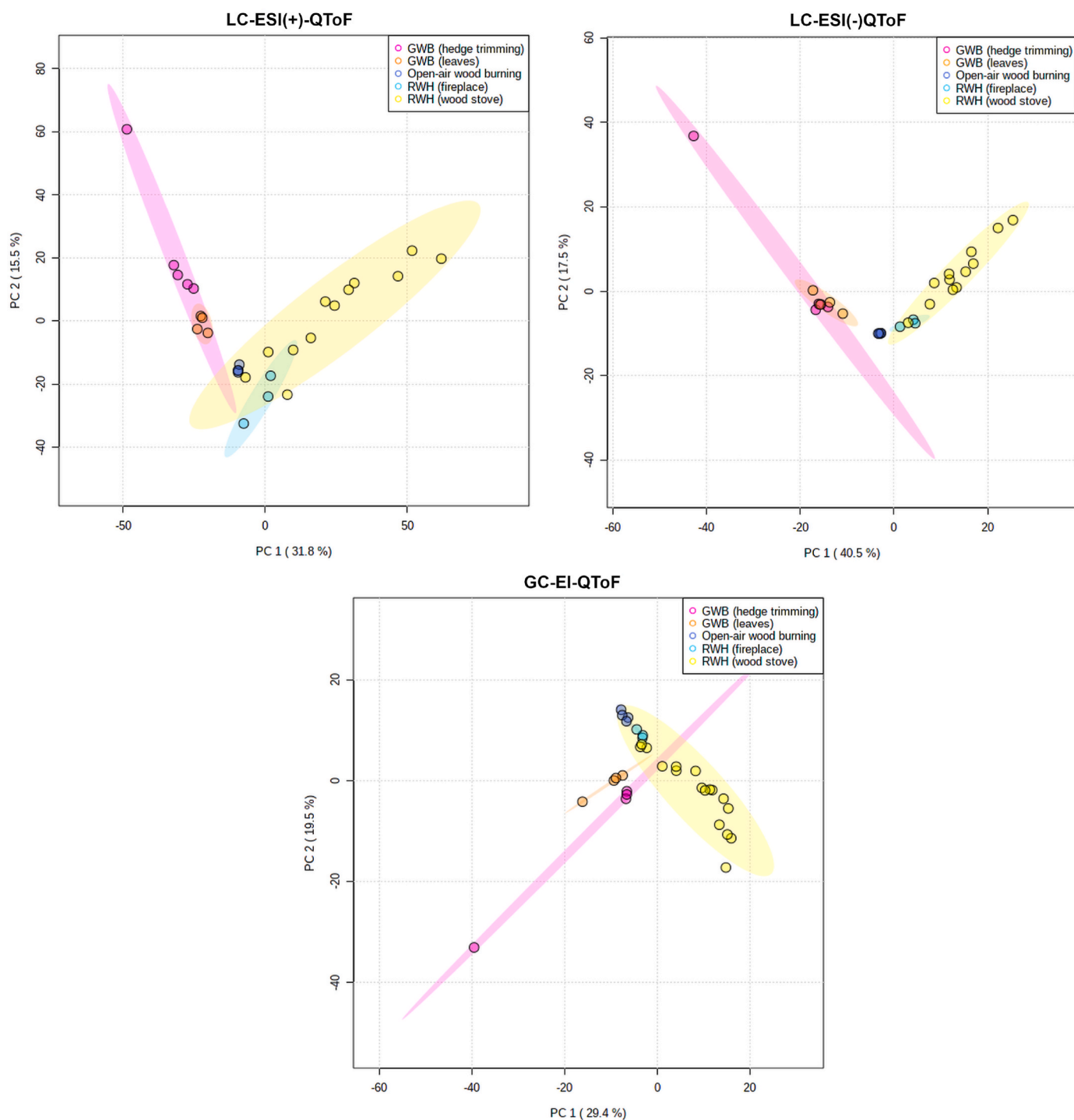


Fig. 1. Principal component analyses (PCA) applied on all biomass burning samples analyzed by LC- or GC-QToF: GWB hedge trimming (in pink), GWB leaves (in orange), open-air wood log burning (in dark blue), residential wood heating with a fireplace (in light blue) and residential wood heating (RWH) with a residential wood stove (all operating conditions, nominal and reduced outputs, dry and humid wood) (in yellow). Data were normalized by TC, the dilution factor and a compensation matrix effect factor calculated using the metsulfuron- d_3 extraction internal standard (EIS) (only for LC-QToF). Ellipses show the 95% confidence interval area.

= 0.938–0.956), and RWH composed of RWS in nominal output experiments (MCE = 0.959–0.964) (Fig. 2, S22–S23). The high abundances observed for sample 848 could explain its distance from other samples of the GWB group. Chemical entities characteristic of GWB, common to both fuels, hedge trimming and fallen leaves, were clearly highlighted on the heatmaps for all datasets. By contrast, entities common to all RWH conditions seemed less numerous than GWB specific entities. These results emphasized the existence of a distinctive and characteristic

chemical composition of RWH and GWB PM emissions.

3.3. Detection of potential RWH and GWB markers

PLS-DA analyses were performed to reveal specific RWH and GWB markers. Both biomass burning sources were separated along the first component (Figs. S24–S25). The values of Q^2 and R^2 determined by LOOCV were respectively 0.82 and 0.87 for LC-ESI(+)-QToF, 0.83 and

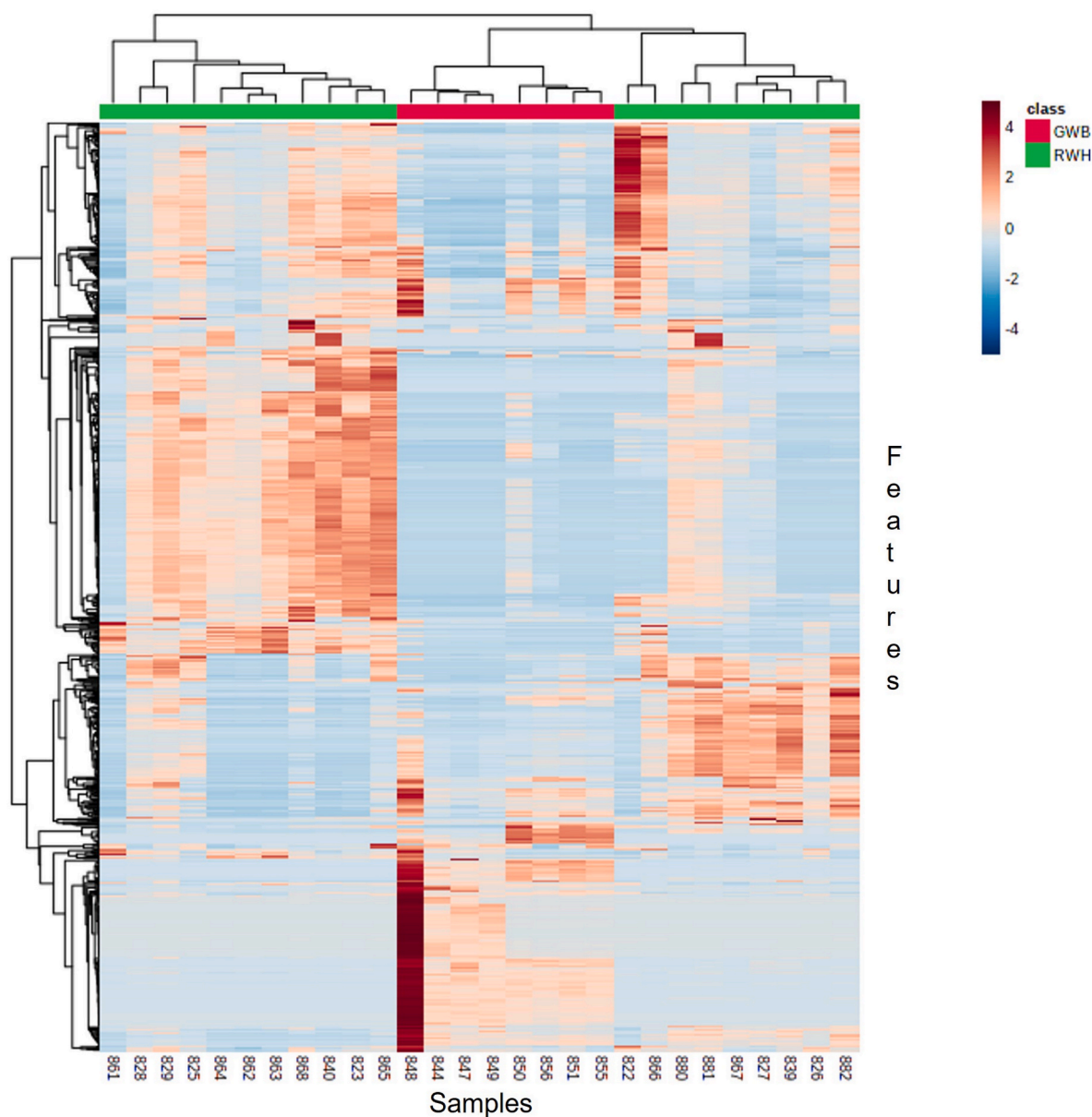


Fig. 2. Hierarchical classification (HCA) and heatmap of residential wood heating (RWH, in green) and green waste burning (GWB, in red) samples using LC-ESI (+)-QToF data. This classification was performed based on the Pearson correlation coefficient using the average linkage method. Normalization by the total carbon (TC), the dilution factor and a compensation matrix effect factor calculated using the metsulfuron- d_3 extraction internal standard (EIS). The color-scale on the right represents the relative abundance of a feature in each sample compared to all samples considered. Results for LC-ESI(-)-QToF and GC-QToF are shown in the SM.

0.87 for LC-ESI(-)-QToF, 0.77 and 0.92 for GC-QToF data, demonstrating good performance of the model. Fig. 3 presents the VIP scores associated to the 30 top ranking features for LC- and GC-QToF results. When a feature was fully associated to a group, the color is red. By contrast, if a feature was absent from a group, the color is blue. A VIP score >1.5 was considered significant. A VIP score >1.5 was observed for 76 features for LC-QToF (50 in ESI(+)) and 26 in ESI(-)) and 47 for GC-QToF. Among them, most of them were specific to GWB and only few, 7 features for LC-ESI(+)-QToF and 2 for the GC-QToF, were specific to RWH. For LC-ESI(-)-QToF data, no specific entity of RWH had a VIP score ≥ 1.5 but 3, with a $1.4 \leq \text{VIP score} \leq 1.5$, were also considered.

All the revealed chemical entities have been individually searched in raw data obtained for GWB, RWH and simultaneous combustion samples to verify their chromatographic responses (resolution, peak height, and shape with minimum 10 points per peak) and the absence of the considered marker in the other combustion group. Only chemical

features with enough abundances (signal intensity $> 10^4$) and/or chromatographic responses have been selected. Finally, 18 possible chemical markers specific of GWB have been discovered from LC-QToF analyses (10 in ESI(+)) and 6 in ESI(-)) and 2 in both modes) and 13 from GC-QToF analyses (Tables 1 and 2). Only, 4 possible markers were determined as specific of RWH (2 in LC-ESI(+)-QToF, 1 in LC-ESI(-)-QToF and 1 for GC-QToF). Fig. S26 to Fig. S30 present the absolute abundance obtained in the samples of GWB, RWH and simultaneous samples. In the simultaneous experiments, the emissions from GWB were dominant compared to the ones from RWH. Abundances of the possible GWB markers were thus comparable in GWB and simultaneous samples. By contrast, the abundances of the potential RWH markers were lower in simultaneous samples than RWH ones alone.

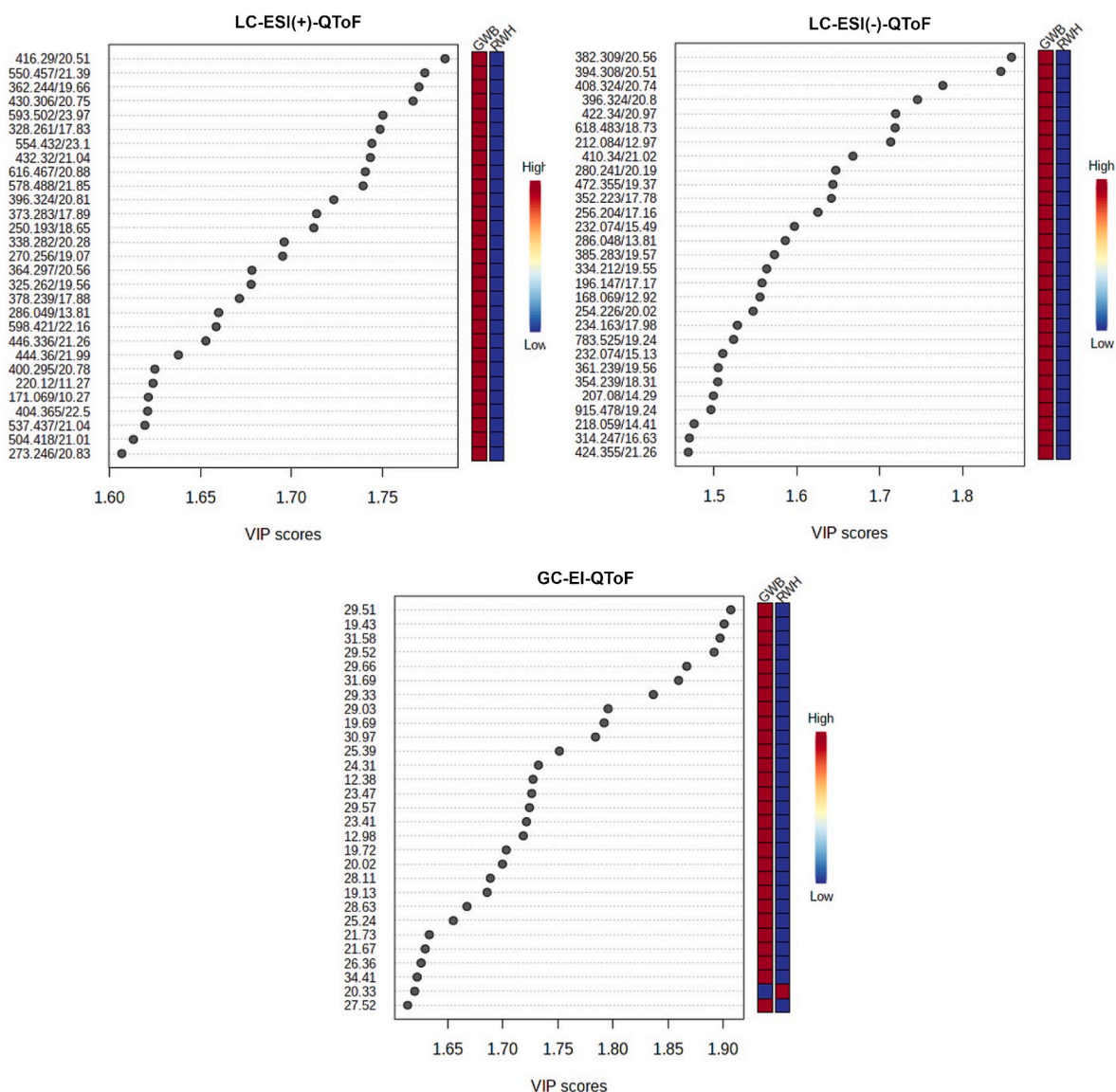


Fig. 3. Chemical feature classification for LC-QToF (left scale: molecular weight (MW) and retention time (RT) as MW/RT) and GC-QToF data (left scale: retention time (RT)) according to the VIP score. The color scale on the right indicates the variation in abundance of the chemical entity (100% = red, 0% = blue) in all samples of both biomass burning sources. Features are sorted by increasing VIP scores. For reading purposes, only the first 30 chemical entities with the highest VIP scores are shown on the graphs.

3.4. Tentative structure identification of the potential markers

Potential formula of the selected LC-QToF markers, which have been confirmed by MS/MS analyses (Figs. S31–S33), are summarized in Table 1. Most of the possible GWB markers are nitrogen-containing organic compounds in agreement with previous studies showing significant contributions of such species in biomass burning aerosols (Bin Abas et al., 2004; Laskin et al., 2009; Mace et al., 2003). Sulfur-containing compounds, such as LC-RWH-1, have been found to be minor components of biomass burning OA (Smith et al., 2009). Four of the possible GWB markers (LC-GWB-1, -13, -16, -17) seem highly specific because they contain at least one chlorine atom. Green waste generally contains higher levels of chlorine (Cl) than wood logs (Kaufmann, 1997; Koppejan and van Loo, 2007) leading to the formation of halogenated species proportionally emitted according to fuel chlorine content (Chandrasekaran et al., 2013a, 2013b).

Six GC-QToF markers, all GWB specific, have been identified from their MS spectra thanks to the NIST database (Figs. S34–S35) (Table 2). LEI spectra produced the detection of the molecular peaks for all of them

(Fig. S36). Tocopherols, (–)-matairesinol, and neophytadiene were validated by injection of native standards. Confirmation of the identity of the two remaining possible markers (oleanol and rimuen) will require standard injections but, to our knowledge, they are not commercially available.

Tocopherols (α -, β -, γ -, and δ -), naturally present in plants, have been observed previously in lignite and tobacco combustion emissions (Nolte et al., 2002; Rybicki et al., 2020) as well as in simulated (including litter, needles, branches, leaves, shrubs, grass, wood, etc.) (Jen et al., 2019; Oros and Simoneit, 2001a) or real wildfire emissions (Alves et al., 2010a, 2011) but also in fireplace emissions for some wood species (notably spruce, mockernut, poplar and oak) (Fine et al., 2001, 2002, 2004a, 2004b) and especially α - and β -tocopherols. The specificity to GWB emissions attributed to δ - and γ -tocopherols is in agreement with previous studies showing higher contents of these substances in senescing leaves (Chrost et al., 1999; Fritsche et al., 2017). Neophytadiene and rimuen are both diterpenes found in plant leaves. They are included in metabolic signaling pathway of plants (Abdel-Aal et al., 2015; Hidayati and Nuringtyas, 2017; Jeng and Huh, 2004; Venkata raman

Table 1
Summary of potential biomass burning molecular markers discovered using LC-QToF analyses.

ID	Median RT (min)	Median MW (g mol ⁻¹)	ESI(+)	ESI(-)	Potential formula	Schymanski's classification
Green waste burning						
LC-GWB-1	11.27	220.120	X		C ₇ H ₁₇ ClN ₆ C ₉ H ₁₉ ClN ₃ O	5
LC-GWB-2	12.96	212.084		X	C ₁₄ H ₁₂ O ₂	4
LC-GWB-3	13.81	194.102	X		C ₁₁ H ₁₄ O ₃	4
LC-GWB-4	13.81	286.049	X	X	C ₁₅ H ₁₀ O ₆	4
LC-GWB-5	14.40	218.059		X	C ₉ H ₁₀ N ₆ O	4
LC-GWB-6	15.62	288.230		X	C ₁₆ H ₃₂ O ₄	4
LC-GWB-7	15.62	310.240	X		C ₁₆ H ₂₈ N ₃ O ₃	4
LC-GWB-8	17.18	196.147		X	C ₁₂ H ₂₀ O	4
LC-GWB-9	17.37	268.203	X		C ₁₆ H ₂₈ O ₃	4
LC-GWB-10	17.37	285.231	X		C ₁₆ H ₃₁ NO ₃	4
LC-GWB-11	19.4	336.231	X		C ₁₆ H ₂₈ N ₆ O ₂ C ₁₈ H ₃₀ N ₃ O ₃ C ₂₀ H ₃₂ O ₄	5
LC-GWB-12	19.56	325.262	X		C ₁₆ H ₃₅ N ₇	4
LC-GWB-13	19.56	361.239		X	C ₁₉ H ₃₆ ClNO ₃	4
LC-GWB-14	19.56	577.471		X	C ₃₅ H ₆₃ NO ₅	4
LC-GWB-15	19.67	362.244	X		C ₁₄ H ₃₂ N ₇ O ₄ C ₁₅ H ₂₈ N ₁₁	5
LC-GWB-16	20.56	364.297	X		C ₂₀ H ₄₃ ClNO ₂	4
LC-GWB-17	20.81	396.324	X	X	C ₁₆ H ₄₃ ClN ₉	4
LC-GWB-18	21.40	550.457	X		C ₃₁ H ₅₆ N ₃ O ₅	4
Residential wood heating						
LC-RWH-1	17.95	442.260		X	C ₂₁ H ₃₈ N ₄ O ₄ S C ₁₅ H ₃₆ N ₇ O ₈ C ₂₉ H ₃₄ N ₂ O ₂	5
LC-RWH-2	19.90	321.265	X		C ₁₈ H ₃₃ N ₄ O C ₁₆ H ₃₁ N ₇ C ₂₀ H ₃₅ NO ₂	5
LC-RWH-3	20.78	292.277	X		C ₂₀ H ₃₆ O	4

et al., 2012; Wang et al., 2013). Emissions of neophytadiene has been also reported during tobacco leaves pyrolysis due possible chlorophyll degradation (Rogge et al., 1994). Both, neophytadiene and rimuen have been only reported in the emissions of simulated wildfires (Oros and Simoneit, 2001b). (-)-Matairesinol belongs to the lignan family (phenylpropane derivatives) (Zhang et al., 2014). Lignans in GWB emissions have been identified previously (Fine et al., 2001; Oros et al., 2006; Simoneit, 2002) but also during wood combustion (Fine et al., 2001, 2002, 2004a, 2004b; Medeiros and Simoneit, 2008; Simoneit et al., 1993; Simoneit, 2002) questioning its specificity as GWB marker. Oleanol (28-Norolean-17-en-3 β -ol) was previously identified as a bioactive triterpene coming from oleoresins of *Pistacia* (Assimopoulou and Papa-georgiou, 2005), which is a common species in shrublands. Similar triterpenic C30 biomarkers (e.g. oleana-2,12-dien-18-oic and olean-12-en-3-ol) have been reported in wildfire emissions (Alves et al., 2010a; Simoneit, 2002). Overall, δ - and γ -tocopherols, along with neophytadiene and rimuen, appear more specific to GWB emissions or wildfires in general.

Identifying the potential markers was challenging and the identification was limited due to lack of specific information related to biomass burning, especially for LC-HRMS, in the existing and explored MS databases (see section 2.5) as well as to the lack of available standard substances. However, even if the number of compounds clearly identified was limited, they have been validated environmentally showing the performance of the aerosolomics based approach applied here.

3.5. Potential abundance of the possible markers in ambient air

A theoretical estimation of the abundance in ambient air of the discovered markers has been done based on the emissions of levoglucosan, a well-known biomass burning marker (Bhattarai et al., 2019; Simoneit et al., 1999). The levoglucosan abundance ratios between RWH (R_{RWH}) or GWB (R_{GWB}) emissions (levoglucosan concentrations for GWB (C_{GWB}) and RWH (C_{RWH}) ranging from 2.0×10^3 to 8.2×10^5 ng m⁻³, depending on the combustible and combustion conditions) (Noblet

et al., 2021) and typical ambient air concentrations observed in France ($C_{AA} = 100\text{--}400$ ng m⁻³ on yearly average) (Golly et al., 2019; Ngo et al., 2018; Weber et al., 2019) have been calculated (Eq. (1) and (2)). A fraction of levoglucosan in ambient air coming from GWB ($F_{GWB AA}$) ranging from 5 to 25%, was assumed, in agreement with previous observations made in Marseille (France) (Salameh, 2015). To estimate the theoretical marker abundance in ambient air, a 24 h sampling duration with a high-volume sampling (30 m³ h⁻¹) and a filter punch of 22 mm diameter (same as NTS analyses) have been considered.

$$R_{GWB} = \frac{C_{GWB} \times F_{GWB AA}}{C_{AA}} \times \frac{1}{24} \quad (1)$$

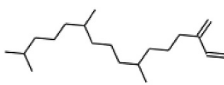
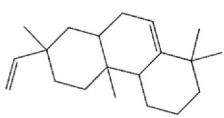
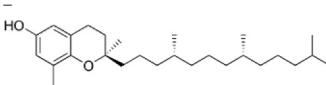
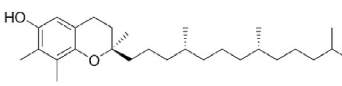
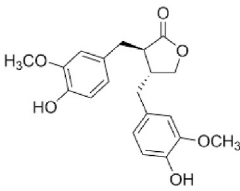
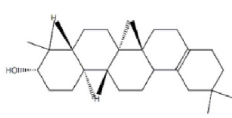
$$R_{RWH} = \frac{C_{RWH} \times (1 - F_{GWB AA})}{C_{AA}} \times \frac{1}{24} \quad (2)$$

Results obtained showed levoglucosan abundance ratios ranging from 1.2 to 47.6 for GWB and from 1.2 to 3.2 for RWH. The expected chromatographic responses of the discovered markers in ambient air samples would be 1 to 50 times lower than those observed here (Figs. S24–S28). Such results support the applicability of the monitoring of the discovered markers in ambient air. The abundance deficit should be compensated by a better selectivity and sensibility usually obtained for targeted analyses.

3.6. Conclusions and implications for PM source apportionment

The comparison of chemical fingerprints obtained by LC- and GC-HRMS led to discover 31 potential markers of GWB and 4 of RWH. If potential molecular formulas and structures have been proposed, their definitive identification will require additional analyses and injection of native standards (if commercially available). Their monitoring in ambient air would be useful for an effective distinction and determination of PM concentrations from RWH and GWB sources. Based on the estimation performed during this work, their ambient concentrations should be sufficient to ensure an accurate quantification. However, their

Table 2
Summary of the potential biomass burning molecular markers discovered using GC-EI-QToF analyses.

ID	RT (min) (RI)	Base peak (<i>m/z</i>)	Potential identification (MW in g mol ⁻¹ , CAS)	Structural formula	Schymanski's classification
Green waste burning					
GC-GWB-1	14.07 (1403)	147.0437	–	–	5
GC-GWB-2	19.13 (1834)	67.0541	Neophytadiene (278.50 g mol ⁻¹ , 504-96-1)		1
GC-GWB-3	19.96 (1914)	257.2259	Rimuen (272.46 g mol ⁻¹ , 1686-67-5)		2
GC-GWB-4	20.19 (1938)	67.0541	–	–	5
GC-GWB-5	21.79 (2103)	151.0750	–	–	5
GC-GWB-6	25.39 (2524)	242.0928	–	–	5
GC-GWB-7	28.43 (2940)	137.0597	δ-tocopherol (402.65 g mol ⁻¹ , 119-13-1)		1
GC-GWB-8	28.62 (2967)	147.1007	–	–	5
GC-GWB-9	29.14 (3046)	151.0754	γ-tocopherol (416.68 g mol ⁻¹ , 7616-22-0)		1
GC-GWB-10	29.48 (3100)	137.0595	(–)-Matairesinol (358.40 g mol ⁻¹ , 580-72-3)		1
GC-GWB-11	29.51 (3103)	193.1004	–	–	5
GC-GWB-12	29.57 (3112)	59.0490	–	–	5
GC-GWB-13	31.58 (3412)	163.1477	Oleanol (412.69 g mol ⁻¹ , 4748-12-3)		2
Residential wood heating					
GC-RWH-1	21.54 (2076)	55.0541	–	–	5

use will be only valid if these compounds are mainly associated to the particulate phase and relatively stable in the atmosphere. Their application to other combustion conditions than those tested here should also be considered, especially in terms of heating devices (pellets stoves), wood species (softwood) and green waste (stubble burning, agricultural waste ...). Indeed, before using them further works will be performed to evaluate their robustness and to refine the choice of the marker candidates to be effectively used for PM source apportionment including the study of their stability, gas/particle partitioning in ambient air and validity/presence for other type of wood species (e.g., softwood). Finally, this research demonstrated the potential of combining of HRMS NTS chemical characterization with multivariate statistical analyses to reveal and identify specific molecular marker candidates of unresolved ambient air PM sources.

CRedit authorship contribution statement

Camille Noblet: Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft,

Writing – review & editing. **François Lestremou:** Conceptualization, Investigation, Methodology, Supervision, Writing – review & editing, Validation. **Serge Collet:** Methodology, Project administration, Writing – review & editing. **Claudine Chatellier:** Investigation, Methodology, Writing – review & editing, Validation. **Jérôme Beaumont:** Investigation, Methodology, Validation, Writing – review & editing. **Jean-Luc Besombes:** Conceptualization, Supervision, Writing – review & editing, Validation. **Alexandre Albinet:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.141242>.

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