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Exploring volatile organic compound emission from thermally modified wood by PTR-ToF-MS†

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Thermal modification of wood is a well-known industrial process performed to increase the durability and dimensional stability or to change the colour of natural wood. The treatment influences many other properties of wood including the emission of volatile organic compounds (VOCs). VOC release ultimately affects the quality of indoor air and the capability of having low VOC emission is often included as a key parameter for the attribution of quality labels. In the present work, wood from six tree species was subjected to different types of treatment and VOC profiling was carried out on both treated and untreated samples by means of PTR-ToF-MS. Different types of thermal treatment were tested, involving either overpressure or vacuum and the effect of different temperature profiles was evaluated. Hardwood and softwood showed different release profiles under all tested conditions: the headspace of softwood was richer in several VOCs, such as terpenes, phenols and C6–C9 aldehydes and carboxylic acids. Upon thermal treatment, terpene emissions decreased, whereas several other VOCs, such as formic acid, formaldehyde, furfural and acetic acid, were released in higher amounts. With its high sensitivity and throughput, PTR-ToF-MS appears to be a very powerful analytical tool, useful in supporting the selection of wood materials for different end uses.

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Introduction

Like most materials, wood releases volatile organic compounds (VOCs) that affect the quality and composition of indoor air, with possible consequences on human and animal health.^{1,2} The US, as well as several European countries, are imposing increasing restrictions on the VOC emissions of wood materials to be used in furniture and construction materials. The European Union published a list of target compounds associated with the lowest concentration of interest values:³ as of December 2021, this list contained nearly 200 individual entries, each corresponding to a compound of possible concern, based on a combination of toxicological and epidemiological data. National institutions within the EU have

adopted analogous lists of compounds and concentrations which are then used to establish guidelines for the attribution of 'EcoLabels'.⁴ Such certifications, even though not mandatory, can be adopted by producers on a voluntary basis and represent an added value in an increasingly environment- and health-conscious market.

VOCs released from wood belong to several different chemical classes. Terpenes and terpenoids are, in terms of relative abundance, the main constituent of the VOC profiles of wood issued from coniferous tree species, also commonly referred to as 'softwood', whereas in wood from deciduous trees (*i.e.* hardwood), terpenes are less abundant or non-detectable.^{5,6} Aldehydes and ketones, carboxylic acids and esters, furans, phenols and aromatic and aliphatic hydrocarbons are other well-represented VOC classes in both hardwood and softwood.^{1,7}

Thermal modification of wood is carried out with the aim of modifying some of its properties. Thermally modified wood is properly defined by the CEN/TS 15679: 2007 standard (thermal modified timber – definitions and characteristics) as "wood in which the composition and physical properties of the cell wall are modified permanently and throughout the thickness of the sawn timber by means of exposure to temperatures above 160 °C in conditions of reduced oxygen availability".

The properties of thermally modified wood (TMW) and the extent of the modification depend on the wood species, the

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type of technology and the process parameters, especially on the maximum treatment temperature. The mass loss (ML) of the lumber because of heat treatment is the main indicator of the intensity of modification. Technologies for the production of TMW are mainly characterized by the way in which the concentration of oxygen is reduced during the treatment. The systems currently used on an industrial scale include superheated steam, nitrogen, vacuum, and oil bath and are patented with different names.⁸

TMW is a greener alternative to chemically treated wood. Compared to the unmodified material, TMW has improved characteristics in terms of dimensional stability, water sorption and resistance to microbial attack. TMW also has a darker colour throughout the thickness, which is appreciated by architects and designers and allows them to substitute expensive tropical timber with local wood species. TMW is particularly amenable to non-structural end-uses such as indoor decking and cladding; however, the impact of thermal treatment on wood VOC emission must also be carefully taken into consideration. Literature data are mostly in agreement in showing that upon thermal treatment terpenes and terpenoids decrease whereas the emission of most of the other VOC classes is promoted. This was observed for Scots pine,^{9,10} southern yellow pine¹¹ and Norway spruce and poplar.¹² A different result was reported by Hyttinen and colleagues,¹³ who found that heat treatment increased furfural but reduced hexanal emission in Norway spruce, Scots pine and European aspen.

Several official methods define methodologies for the measurements of VOCs emitted by construction and furniture materials. These entail the use of test chambers¹⁴ or test cells.¹⁵ Air and volatiles are swept into a thermal desorption (TD) tube, which is analysed by TD coupled to gas chromatography-mass spectrometry (GC-MS). The size of the chambers (typically 1–30 m³) and the need to sample manually limit the analytical throughput of this approach. Even though sampling using TD tubes is the most widespread technique for the study of wood emission, other sample prep protocols have been adopted in association with GC-MS, such as solid-liquid extraction,¹⁶ static and dynamic headspace,^{6,17} solid-phase microextraction,¹⁸ accelerated solvent extraction¹⁹ and direct remote sampling using passivated canisters, followed by TD-GC-MS.²⁰ All these approaches are limited in throughput because GC-MS analysis, and sometimes sample pre-treatment, are time consuming steps. Studies published so far have often been restricted to one to three different species, sometimes focusing on a single tree and wood type (*i.e.*, either deciduous trees/hardwood or coniferous trees/softwood). Direct comparison between literature works, albeit possible, is made difficult by the fact that when different sample prep techniques are used, the respective ranges of sampled compounds will only be partially overlapping. Finally, it must be noted that most studies ignore potentially health-relevant VOCs emitted by wood such as methanol, acetaldehyde, formic acid and formaldehyde, because due to their chemical-physical characteristics, these are not retained – or poorly

retained – by the Tenax-based sorbents used in the majority of TD tubes.²¹

PTR-ToF-MS has previously been used to discriminate untreated wood core samples originating from 14 different tree species based on their VOC profiles.²² The present work is the first example of the application of proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) to the analysis of thermally treated wood. VOCs emitted by wood originating from six different tree species were analysed, including both softwood (Norway spruce and Scots pine) and hardwood (beech, ash, oak and tulipier). The work also investigates VOC emission by TMW samples obtained by two patented heat-treatment processes (Styl⁺wood® and Thermo-vacuum®) based on different technologies and also varying temperature profiles. Whenever possible, VOC emissions by wood samples originating from different types of plant tissue (*i.e.*, sapwood *vs.* heartwood) were compared. The rapidity of analysis provided by the direct-injection mass spectrometry technique allowed for the intercomparison of VOC emission profiles within a relatively large sample set. Since PTR-ToF-MS does not need any pre-concentration or derivatisation, direct determination of formic acid, methanol, formaldehyde and acetaldehyde was also possible. Overall, this study presents a comprehensive picture of the VOC profile of a wide range of native wood and TMW, proving that PTR-ToF-MS is a potentially powerful tool to support decision-making in the development and production of TMW products for different end-use products.

Materials and methods

Thermal treatment

The Styl⁺wood® technology (henceforth named SW) is a new thermal modification process entering the market, developed by BigOnDry Srl (Castione, Italy). In this system, the oxygen in the reactor is excluded by means of a slight overpressure produced by the gases released by wood pyrolysis and, if needed, by the injection of a small quantity of saturated steam. The process is controlled by software which considers different inputs such as the oxygen concentration, the pressure, and the temperature difference between the core of the wood and the surrounding air. According to Hill⁸ it is classified as a wet close system, even if it is actually a semi-wet system since the moisture in the reactor during the process is lower than in systems with saturated steam or superheated steam. In the framework of the present research project, technological properties of SW products including VOC emissions were investigated.

The Thermo-vacuum® technology (henceforth named TV) is a thermal modification process where a low oxygen concentration is provided by vacuum and it is characterised by convective heat transfer. The system has been extensively described in previous papers.^{23,24} According to Hill⁸ it is classified as a dry open system since during the modification stage it does not make use of any source of vapour. In addition, the

on-off activity of the vacuum pump continuously removes from the reactor all volatile compounds that contribute to accelerating the degradation of polysaccharides in the wood cell wall. In theory, this should lead to lower mass loss and VOC emission compared to SW.²⁵

In the present study, variation of VOC emission from wood due to thermal modification was investigated. The analysis was carried out in five different SW and one TV modification batches. Each batch was composed of a mixed stack containing sawn boards of the wooden species analysed. Fig. 1 presents the temperature profiles of the thermal treatments: they are characterized by the maximum temperature reached (T_{\max}) and by the relative area (H). H [h °C], which is calculated from the temperature profile vs. time and represents the quantity of effective heat power exchanged during the treatment process linearly correlated with the wood mass loss (ML), which is a true indicator of the modification intensity. Table 1 presents a summary of the process parameters.

The SW modification batches named A, B, C, and D have different T_{\max} values (160°, 185°, 200° and 215 °C). The SW modification batch named E has the same T_{\max} value of D (215 °C) but a faster T rate during heating. The TV modification batch has the same T_{\max} value (215 °C) and the same H value as the SW batch named D. In the framework of such an experimental matrix, batches A, B, C, and D allow for the evalu-

ation of the influence of T_{\max} ; batches D and E allow for the evaluation of the influence of time and batches D and TV show the differences between SW and TV.

Wood sampling

Each treatment batch was composed of approximately 1 m³ of sawn boards (30 mm thick) of six species, which are among the most widespread on the TMW market for furniture, flooring, joinery, and decking (Table 2).

A portion of the board of each species was kept untreated as a reference.

The mass of each treated board oven dried before the treatment (M_0) and after the treatment (M_{ht}) was measured and the mass loss was calculated as:

$$ML = \frac{(M_0 - M_{ht})}{M_0} \%$$

After the treatment, in order to minimize the effect of time on emissions, sampled treated boards and reference boards (1 + 1 boards from each species) have been conditioned for about two months in a climatic chamber at RH 65%, T 20 °C. After the conditioning, the equilibrium moisture content of the wood was about 12% in untreated samples and about 6% in treated samples. Such reduced hygroscopicity is peculiar to thermally modified wood and it is due to the thermal degradation of hemicellulose and cellulose in the cell walls.

Five mm of thickness were removed from the external surface. In addition, some shavings from the last planar step to a depth of 55 mm were collected and immediately placed in a clear vial and capped.

PTR-ToF-MS measurements

All measurements were performed using a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH,

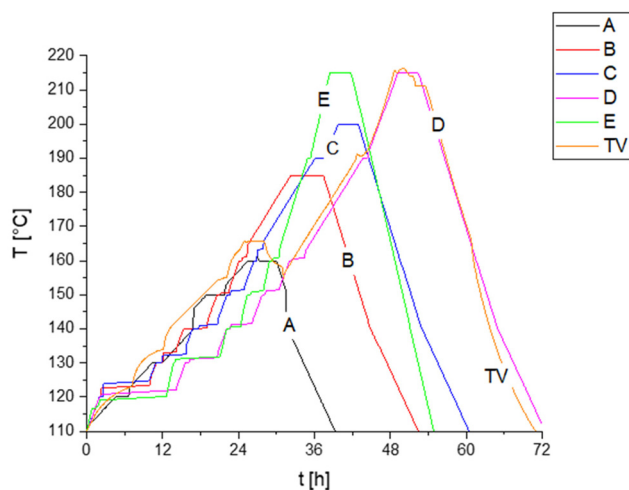


Fig. 1 Temperature profiles of the thermal treatments. A, B, C, D and E all refer to different SW modification batches.

Table 2 Description of samples (S: softwood; H: hardwood; d: wood with differentiated heartwood)

Species	Species ID	Oven-dry density	Notes
Norway spruce (<i>Picea abies karst</i>)	AR	388 kg m ⁻³	S
Scots pine (<i>Pinus sylvestris</i> L.)	PS	592 kg m ⁻³	S, d
Beech (<i>Fagus sylvatica</i> L.)	FG	690 kg m ⁻³	H
Ash (<i>Fraxinus</i> spp.)	FR	707 kg m ⁻³	H
Oak (<i>Quercus</i> spp.)	RV	745 kg m ⁻³	H, d
Tulipier (<i>Liriodendron tulipifera</i>)	TP	537 kg m ⁻³	H, d

Table 1 Process parameters and final mass loss (T_{\max} = maximum temperature, H_{132} = relative area, ML% = percentage mass loss)

Batch	T_{\max} [°C]	H_{132} [h °C]	ML % (ash)	ML % (beech)	ML % (oak)	ML % (tulipier)	ML % (spruce)	ML % (pine)
A	160	362	0.8	1.0	2.1	1.1	0.9	1.0
B	185	972	4.3	3.1	5.3	3.1	2.1	2.6
C	200	1397	8.8	6.7	8.7	6.2	3.4	4.3
D	215	1858	13.1	12.2	11.9	11.1	6.1	6.6
E	215	1307	12.0	9.9	12.0	9.9	5.7	5.7
TV	215	1845	12.6	10.0	12.4	10.0	6.2	7.0

Innsbruck, Austria). The ionisation conditions were as follows: 560 V drift voltage, 110 °C drift temperature, and 2.80 mbar drift pressure, resulting in an E/N ratio of 130 Td. Data acquisition was set to record one mass spectrum per second. Inlet flow was set to 40 sccm.

Three replicates of 0.5 g of each sample were placed in a 20 ml screw-capped clear vial (Supelco, Bellefonte, US). The vials were equilibrated at 40 °C for 30 min before the analysis. Each measurement was the averaged result of 30 seconds of acquisition. During sample measurement, no significant decrease in the primary ion amount, as estimated by monitoring ion m/z 21.022, was observed, which indicates that no primary ion depletion took place at any moment.

Automated headspace analysis was carried out by means of a customized multipurpose autosampler (Gerstel GmbH, Mulheim am Ruhr, Germany). The autosampler was equipped with a 2.5 mL headspace syringe, and a multiple headspace extraction (MHE) tool which was connected to the PTR-MS inlet. At the moment of analysis, the robotic arm would pick up the MHE tool and pierce the vial septum; during measurement, the air sampled by PTR-MS would be replaced by clean air, supplied through the headspace syringe.

Data extraction and analysis

Dead time correction, internal calibration of PTR-ToF-MS data and subsequent peak extraction steps were performed according to procedures described elsewhere^{26,27} to reach in most cases a mass accuracy of ≤ 0.001 Th, which is sufficient for sum formula determination. The baseline of the mass spectra was removed after averaging the whole measurement and peak detection and peak area extraction was performed by using a modified Gaussian to fit the data. Whenever a peak was detected, the volatile concentrations were calculated directly *via* the number of detected ions in ppbV (part per billion in volume) levels according to the formulas described by Lindinger *et al.* (1998)²⁸ by assuming a constant reaction rate coefficient ($k_R = 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). For H_3O^+ as a primary ion, this introduces a systematic error for the absolute concentration for each compound that is in most cases below 30% and can be accounted for if the actual rate constant is available.²⁹ Mass spectra were recorded in the mass-to-charge ratio range of 15–300 Th. PTR-ToF-MS data processing and statistical analyses were performed by using software packages and scripts developed in-house in MATLAB (MathWorks, Natick, MA) and R Programming Language.³⁰

Results and discussion

Overall, the sample set consisted of six different tree species subjected to six different treatments or untreated. Whenever possible, samples originating from different wood types of the same species (*i.e.* heartwood *vs.* sapwood) were separately processed and characterised. The characteristics of the sample set are summarised in Table 3.

Table 3 Sample set: available samples grouped according to tree species, wood type and treatment (X = available, n.a. = not available)

Tree species	Wood type	Treatments						
		NT	A	B	C	D	E	TV
AR	Whole	X	X	X	X	X	X	X
PS	Whole	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	X
PS	Sapwood	X	X	X	X	X	X	n.a.
PS	Heartwood	X	X	X	X	X	X	n.a.
FG	Whole	X	X	X	X	X	X	X
FR	Whole	X	X	X	X	X	X	X
RV	Whole	n.a.	X	n.a.	n.a.	X	n.a.	X
RV	Sapwood	X	n.a.	X	X	n.a.	X	n.a.
RV	Heartwood	X	n.a.	X	X	n.a.	X	n.a.
TP	Whole	n.a.	X	n.a.	n.a.	n.a.	n.a.	X
TP	Sapwood	X	n.a.	X	X	X	X	n.a.
TP	Heartwood	X	n.a.	X	X	X	X	n.a.

The whole PTR-ToF-MS dataset consisted of 289 for softwood and 300 mass peaks for hardwood (*i.e.*, the 289 found in softwood, plus 11 additional ones). After additional inspection of the dataset, mass peaks with headspace concentration of < 1 ppbV were excluded, along with redundant data (^{13}C isotopologues and water adducts). This eventually resulted in 99 mass peaks, common to both hardwood and softwood. For some very abundant VOCs, signal saturation of the ^{12}C isotopologue mass peak was observed: we therefore used the ^{13}C isotopologue and used theoretical isotopic abundance to extrapolate the actual headspace concentration. This extrapolation was performed for mass peaks m/z 138.137 (monoterpenes), m/z 62.032 (acetic acid), m/z 46.036 (acetaldehyde), m/z 34.037 (methanol), and m/z 98.031 (furfural).

Fig. 2 provides a graphic representation (heatmap) of all VOC profiles, where samples and mass peaks are grouped by means of hierarchical cluster analysis and sorted accordingly. In the heatmap, closely clustered columns represent wood samples that are similar in terms of VOC emission. A major separation is highlighted between untreated and treated samples, placed on the left- and right-hand side of the heatmap, respectively. This is not surprising, since during thermal treatment, several processes take place modifying the release profile: some VOCs are lost or reduced by evaporation, while others are increased as a result of improved extractability from the wood tissue or generated *ex novo* by the thermally induced transformation of non-volatile wood compounds.

Looking at unmodified wood samples (NT), these can be roughly subdivided into softwood (AR, PS) and hardwood (FG, FR, RV, TP) based on their VOC profiles, with the former displaying higher overall emission. As for TMW, cluster analysis also highlights the separation between softwood and hardwood. The evolution of VOC profiles with thermal treatment is in agreement with the literature:⁷ in softwood some VOCs decrease while others increase whereas in hardwood, which had lower overall emissions, several VOCs increase significantly.

In order to support accurate mass-based tentative identification of the VOCs obtained in the wood sample headspace

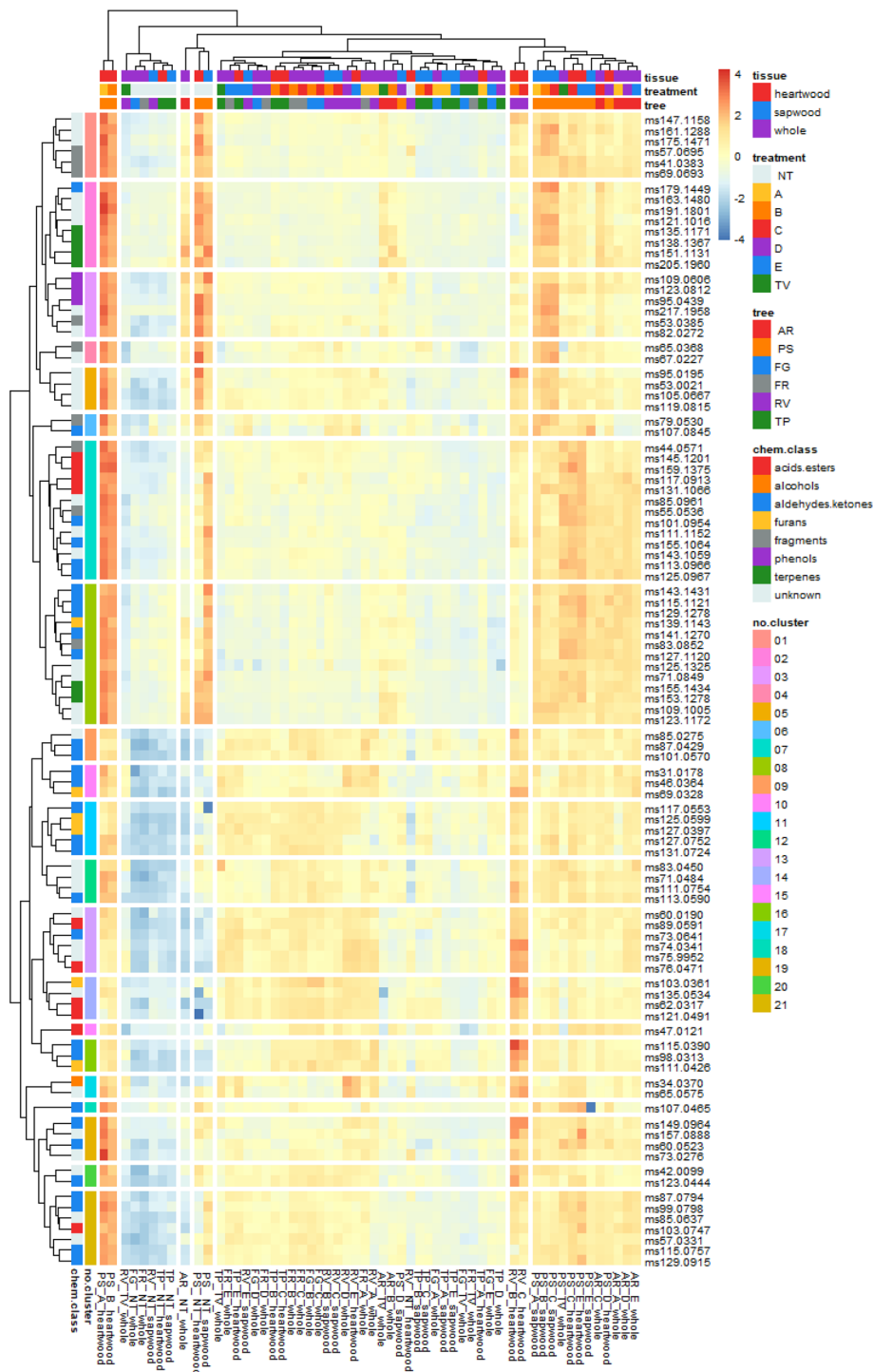


Fig. 2 Heatmap of wood headspace VOC profiles. Data are log transformed, autoscaled and centered. Rows represent mass peaks and columns represent samples, averaged over all analytical replicates.

using PTR-ToF-MS, we conducted cross-platform validation using SPME-GC-MS on a subset of the samples. Whenever possible, SPME-GC-MS data were used to support tentative identifications: a complete list of the mass peaks with respective tentative identifications is supplied in ESI – S1.†

In the heatmap, closely clustered rows represent VOCs that display similar behaviour across all samples. Interestingly, VOCs belonging to the same chemical class are often clustered together or occupy neighbouring clusters: this indicates that compounds that are chemically alike respond similarly to thermal treatment, and possibly have similar origins. Looking

at the cluster structure, a subdivision into two major groups can be highlighted, occupying the upper and bottom half of the heatmap, respectively. Within each of these large subdivi-

Table 4 Mass peaks mentioned in the text, with the corresponding tentative identifications. Highlighted mass peaks are also presented in Fig. 3 and 4

Meas. mass	Theor. mass	Sum formula	Tentative identification
138.137	138.136	$[C_9^{13}CH_{16}]H^+$	Monoterpenes
205.196	205.195	$[C_{15}H_{24}]H^+$	Sesquiterpenes
95.044	95.049	$[C_6H_6O]H^+$	Phenol
109.061	109.065	$[C_7H_8O]H^+$	2-Methyl-phenol
123.081	123.080	$[C_8H_{10}O]H^+$	2,3-Methyl-phenol
101.095	101.096	$[C_6H_{12}O]H^+$	Hexanal
115.112	115.112	$[C_7H_{14}O]H^+$	2-Heptanone
127.112	127.112	$[C_8H_{14}O]H^+$	2-(<i>E</i>)-Octenal
141.127	141.127	$[C_9H_{16}O]H^+$	2-(<i>E</i>)-Nonenal
143.143	143.143	$[C_9H_{18}O]H^+$	Nonanal
117.091	117.091	$[C_6H_{12}O_2]H^+$	Hexanoic acid
131.107	131.107	$[C_7H_{14}O_2]H^+$	Heptanoic acid
145.120	145.122	$[C_8H_{16}O_2]H^+$	Octanoic acid
159.137	159.138	$[C_9H_{18}O_2]H^+$	Nonanoic acid
47.012	47.013	$[CH_2O]H^+$	Formic acid
62.032	62.032	$[C^{13}CH_4O_2]H^+$	Acetic acid
31.018	31.018	$[CH_2O]H^+$	Formaldehyde
46.036	46.037	$[C^{13}CH_4O]H^+$	Acetaldehyde
34.037	34.037	$[^{13}CH_4O]H^+$	Methanol
98.031	98.032	$[C_4^{13}CH_4O_2]H^+$	Furfural
111.043	111.044	$[C_6H_6O_2]H^+$	5-Methyl-furfural

sions, minor groupings could be highlighted: these are labelled clusters 1–21 in Fig. 2 and are referred to as such. In the following paragraphs, the behaviour of the different VOCs according to the respective chemical classes is discussed: a list of representative mass peaks with the respective tentative identifications is provided in Table 4 and for some of these mass peaks, boxplot representations of the results are provided in Fig. 3 and 4. The complete results are instead provided in ESI – S2.†

The upper half of the heatmap (Fig. 2, clusters 1–8) includes compounds that are more concentrated in softwood, in either NT or TMW, or in both.

Cluster 2 contains several mass peaks which can be assigned to terpenes. In coniferous species these compounds are stored in resin canals, where they remain readily accessible³¹ and make up most of the softwood VOC emission profile; this is not observed for deciduous tree species, which instead lack resin canals. Thanks to terpenes, softwood gives off a pleasant smell that has been reported to improve mood and reduce stress³² even though desirable properties must be carefully weighed against potentially harmful effects as terpenes are known irritants and the EU includes them in the list of compounds of potential concern for construction material emission. Mass peak m/z 138.137 represents the sum of monoterpenes. We observe that in Scots pine monoterpenes alone account for more than 80% of total emission; their levels remain relatively unaltered in the range $T = 160$ – 185 °C, showing a sharp drop of two orders of magnitude when $T =$

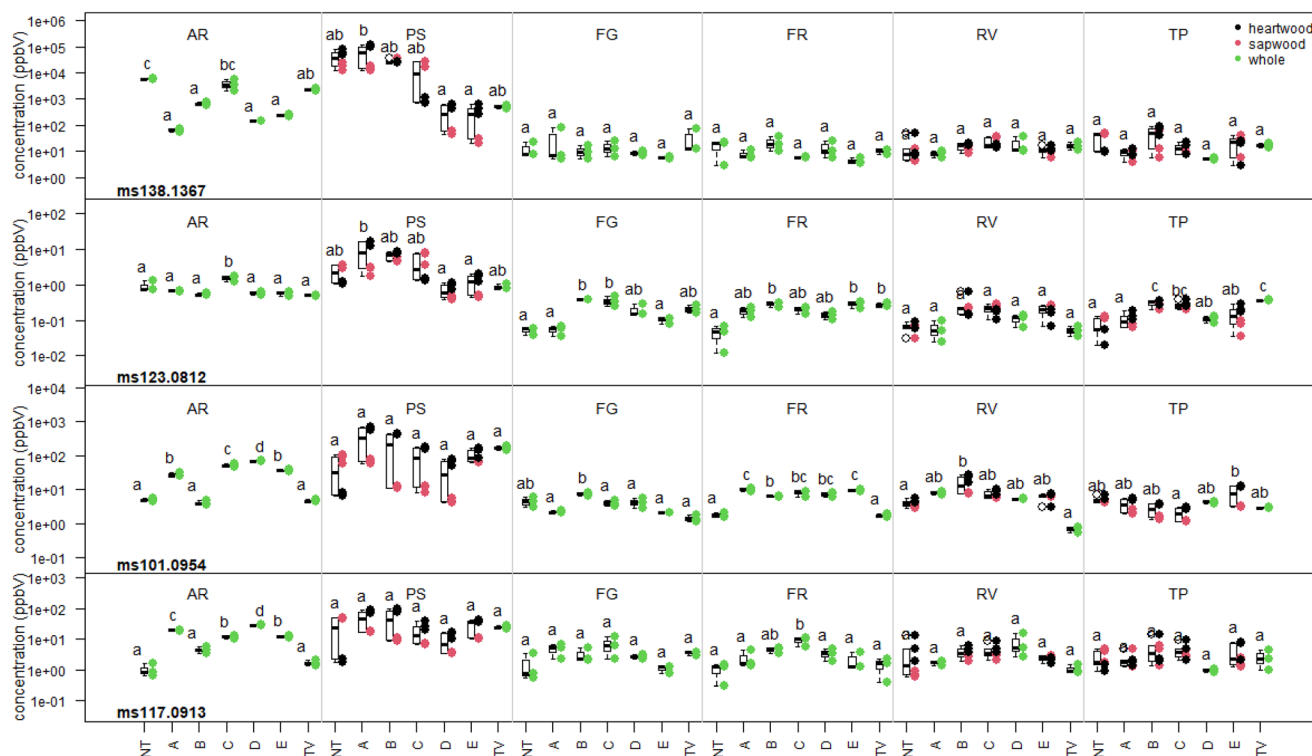


Fig. 3 Boxplots for selected mass peaks. Letters indicate significant differences (Tukey's *post hoc* test, $p < 0.01$).

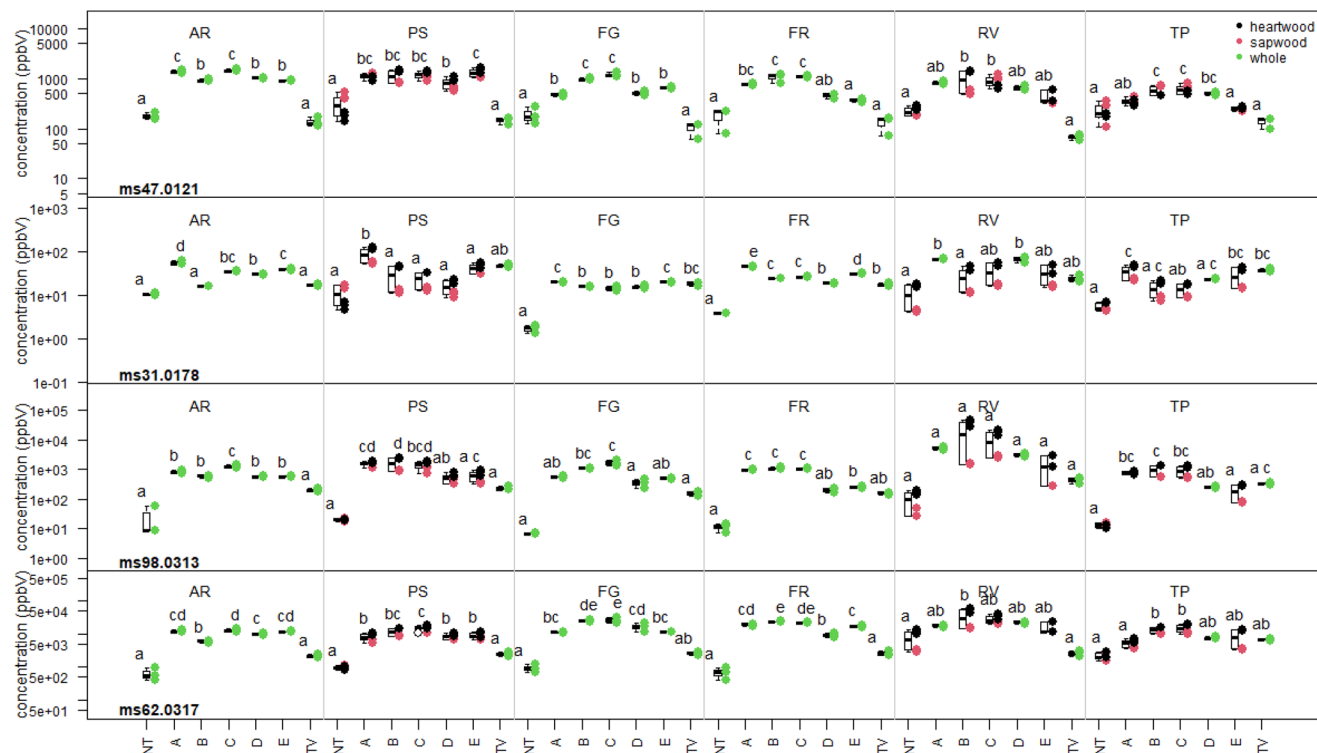


Fig. 4 Boxplots for selected mass peaks. Letters indicate significant differences (Tukey's *post hoc* test, $p < 0.01$).

200–215 °C (Fig. 3). It is well known that thermal treatment speeds up the release of terpenes from wood, causing a drop in their emission.³³ In Norway spruce any thermal treatment always results in a significant decrease in terpene emissions with the exception of $T = 200$ °C (treatment C). Mass peak m/z 205.196 is also relevant to terpene chemistry as it can be assigned to sesquiterpenes, which can be detected at high concentrations in the headspace of softwood samples and react to thermal treatment similarly to monoterpenes (ESI – S2†). In a previous research work²² conducted using PTR-ToF-MS on untreated wood cores, mass peaks m/z 137 and 205 were also found to be important in discriminating between coniferous and deciduous species. As for hardwood, mono- and sesquiterpene peaks are detectable, but at levels typically 100 000-fold lower than those observed for softwood. These are likely due to negligible cross contaminations between different sample types, that possibly occurred during preparation. PTR-ToF-MS does not allow for the speciation of terpenes, unless a GC separation step is coupled to it.³⁴ Based on SPME-GC-MS data, mass peak m/z 138.137 can be associated with monoterpenes alpha- and beta-pinene, camphene, D-limonene and delta-carene and mass peak m/z 205.196 to sesquiterpenes alpha-murolene, beta-isocaryophyllene and longifolene (ESI – S2†).

Volatile phenols are found in cluster 5. Their emissions are expected to increase as a result of the thermal degradation of lignin. Phenol and structurally related compounds are measured in the headspace of thermally treated white poplar,¹² Chinese white poplar¹⁷ and Tunisian softwood

species.³⁵ Among all volatile phenols, phenol presents the highest toxicological concern with documented adverse effects on exposed workers.³⁶ PTR-ToF-MS detected mass peaks m/z 95.044 (phenol), m/z 109.061 (2-methyl-phenol) and m/z 123.081 (2,3-methyl-phenol). Fig. 3 shows the headspace concentration of 2,3-methyl-phenol across all samples: in NT wood, PS shows the highest concentrations; indeed, volatile phenols have been reported as odor-active compounds in untreated Scots pine.³⁷ Untreated hardwood displayed instead very low (<1 ppbV) volatile phenol emissions whereas in TMW, phenol concentration dependency on temperature followed a bell-shaped curve, peaking at $T = 180$ – 200 °C (B–C) and decreasing for $T = 215$ °C (D).

PTR-ToF-MS also detected mass peaks corresponding to several aliphatic aldehydes and ketones from C6 to C9 (cluster 7–8 in Fig. 2 and Table 4), and C6–C9 carboxylic acids (cluster 7 in Fig. 2 and Table 4). When long-chain fatty acids undergo autoxidation, the generation of a wide range of volatile aldehydes is to be expected; aldehydes then undergo further oxidation into carboxylic acids.³⁸ In wood VOC emission studies, hexanal is most commonly detected whereas aldehydes with more than six carbon atoms are only rarely reported.^{17,35} Little information is available about the corresponding carboxylic acids. Even though the impact of these aldehydes and acids is minor from the human exposition standpoint, the fact that they are consistently detected in wood samples from several tree species extends our current knowledge on wood VOC emission and provides a window into wood thermal degra-

dation kinetics. Aldehydes/ketones and acids are more concentrated in softwood than in hardwood. Fig. 3 graphically presents the results for hexanal (m/z 101.095) and hexanoic acid (m/z 117.091). Hexanal release is significantly affected by thermal treatment in 5 out of 6 tree species, whereas for hexanoic acid the effect is less evident: this likely reflects the fact that aldehydes are more volatile than the corresponding acids.

The lower half of the heatmap (Fig. 2, clusters 9–21) includes compounds whose concentration is similar for both softwood and hardwood, and increases following thermal treatment.

Similar trends are observed for formic acid (m/z 47.012, cluster 15 in Fig. 2 and 4), and acetic acid (m/z 62.032, cluster 14 in Fig. 2 and 4). Formic acid – even though its formation can be expected from wood thermal treatment – is poorly reported. In fact, it is difficult to analyse formic acid by TD-GC-MS due to the high volatility of this compound. PTR-ToF-MS allows bypassing this problem. Acetic acid comes from the degradation of hemicelluloses and lignin. This VOC is well-represented in terms of relative abundance within the headspace of untreated wood, reaching 60% of total VOC emission in NT oak. Looking at NT samples only, oak and tulipier show the highest acetic acid release (Fig. 4): this is likely related to the fact that in hardwood lignin and hemicelluloses show a higher degree of acetylation.^{6,13,39,40}

Formaldehyde (m/z 31.018, cluster 10 in Fig. 2 and 4) is often reported as wood VOC and it is formed following the degradation of lignin and polysaccharides. Formaldehyde is a recognised carcinogen⁴¹ and therefore raises the most serious health concerns among all wood VOCs. Standard methods have been developed for formaldehyde determination in construction materials, which require derivatisation, followed by liquid chromatography or photometric determination.⁴² As previously stated, TD-GC-MS is not suited to formaldehyde determination; therefore, the fact that PTR-ToF-MS allows for measurement in a direct, sensitive and rapid fashion is of particular interest: formaldehyde quantification by PTR-MS is possible, provided the relative humidity of the sample is known.⁴³ In our dataset, important differences in formaldehyde emission among tree species were highlighted (high emission in AR, PS, RW, and TP while low emission in FG and FR). Concentrations readily increased upon heating in TMW, starting from $T = 160$ °C. Interestingly, PTR-ToF-MS was also capable of directly determining acetaldehyde (m/z 46.036, cluster 10) and methanol (m/z 34.037, cluster 17), which, like formaldehyde, are toxic and not easy to detect by TD-GC-MS.

Cluster 16 contains furfural (m/z 98.031, Fig. 4) and 5-methyl-furfural (m/z 111.043). These are well-known products of thermal degradation of hemicellulose and increase upon thermal treatment in both hardwood and softwood.^{11,17,35} Relatively weak evidence of carcinogenicity is reported for furfural.⁴⁴ Our results confirm strong dependence on temperature for furfural and 5-methyl-furfural formation: release peaks at $T = 180$ – 200 °C, but 160 °C is enough to elicit a sharp increase with respect to NT samples. Oak shows the highest levels among the tested tree species.

In Scots pine (PS) and oak (RV), heartwood and sapwood were sampled separately. In either case, there is a striking difference in VOC release between wood types. The heatmap (Fig. 2) shows that for untreated PS and RV heartwood and sapwood cluster together but in TMW heartwood and sapwood behave differently. For heartwood PS, treatments A and B ($T = 160$ and 180 °C) show high release for many VOCs, in particular terpenes, phenols, fatty acids and aldehydes (including formaldehyde). Heartwood RV treatments B and C ($T = 180$ and 200 °C) form a separate cluster from all other hardwood samples (Fig. 2), displaying higher than average VOC release, particularly for acetic acid and furfural (Fig. 4).

Previous research^{10,45} has already highlighted that Scots pine heartwood releases more VOCs than sapwood, probably as a result of a higher extractive content. Less information is instead available on the difference in VOC release in deciduous trees according to tissue type and the findings reported in this work strongly support the choice of oak TMW sapwood over heartwood as a construction material.

Finally, the effect of some technological parameters was investigated. The Styl⁺wood® (SW) process with $T_{\max} = 215$ °C (treatment D) was compared with the Thermo-vacuum® process (TV) using the same temperature ramp. Previous work²³ shows that TV affords materials with improved properties in terms of dimensional stability and durability. PTR-ToF-MS analysis reveals several significant differences in VOC release between TV and SW, but the results are often species-dependent. For example, TV, which is an open system, is more effective in reducing the generation of acetic acid in all tree species except TP and formaldehyde in AR and RV, whereas for furfural TV is more effective than SW in AR, less effective in TP (Fig. 4). A comparison of SW treatment E with treatment D (same $T_{\max} = 215$ °C but a faster ramp, Fig. 1) was carried out with the purpose of examining the effect on VOC release of the fine-tuning parameter of the Styl⁺wood® process. In this case, the impact of the faster temperature ramp is minimal and in cluster analysis D and E samples from the same tree species always appear closely grouped (Fig. 2).

In the present work, extensive PTR-ToF-MS profiling was carried out on shavings from six different wood species under native conditions and after six different types of thermal treatment. This is the first example of the use of PTR-ToF-MS for the analysis of thermally modified wood. The rapidity of analysis allowed us to perform comparisons across a relatively large sample set, combining different tree species and treatments. The effect of some variables, such as the use of vacuum, changes depending on the tree species they are applied to; therefore, results obtained on a single tree species cannot always be extrapolated to all types of wood: this further substantiates the usefulness of high-throughput analytical techniques, allowing the rapid measurement of large sample sets and thus evaluation of the effect of combinations of several parameters.

The capability of PTR-ToF-MS to directly determine some very volatile compounds, such as formaldehyde, is also noteworthy, as the measurement of such compounds normally

calls for dedicated methods, requiring complex sample preparation.

All the characteristics mentioned so far highlight the applicability of PTR-ToF-MS in the characterization of wood materials at different stages of the production line, for example during the thermal treatment process on the chimney with the aim of controlling pollution or to optimise process parameters, as well as VOC monitoring from TMW on a post-production line for quality inspection and labelling.

Conflicts of interest

There are no conflicts to declare.

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