

VOLATILE ORGANIC COMPOUNDS EMITTED FROM UNTREATED AND THERMALLY MODIFIED WOOD—A REVIEW

Jure Pohleven

Researcher
InnoRenew CoE
SI-6310 Izola, Slovenia
and
University of Primorska
Andrej Marušič Institute
SI-6000 Koper, Slovenia
E-mail: jure.pohleven@innorenew.eu

Michael D. Burnard†*

Deputy Director
InnoRenew CoE
SI-6310 Izola, Slovenia
and
Assistant Professor
University of Primorska
Andrej Marušič Institute
SI-6000 Koper, Slovenia
E-mail: mike.burnard@innorenew.eu

Andreja Kutnar†

Director
InnoRenew CoE
SI-6310 Izola, Slovenia
and
Associate Professor
Faculty of Mathematics
Natural Sciences and Information Technologies
University of Primorska
Andrej Marušič Institute
SI-6000 Koper, Slovenia
E-mail: andreja.kutnar@innorenew.eu

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Abstract. Volatile organic compounds (VOCs) are a diverse group of compounds that can have a strong impact on indoor air quality. Wood and thermally modified wood emit VOCs, which are referred to as wood VOCs, and can elicit various negative or positive effects in different organisms, including humans. Wood is a complex multicomponent biopolymer with inherent variability, which is also reflected in the emissions of VOCs. Variability in wood VOC emissions has been attributed to endogenous and exogenous factors, such as wood species, type of wood sample, wood treatment, etc. Nevertheless, studies have reported reasonably consistent results regarding VOC emissions from individual (thermally modified) wood species. Softwoods emit the highest concentrations of wood VOCs composed primarily of volatile terpene emissions (70-90%) and lower concentrations of hexanal and acetic acid (10-25%). VOC emissions from hardwoods are considerably lower (approximately 50 times) and include hexanal and pentanal, acetic acid, as well as other VOCs formed during wood degradation processes, but not volatile terpenes. Total VOC emissions from softwoods are reduced following thermal treatment, whereas emissions are increased from hardwoods after thermal treatment. In thermally

* Corresponding author

† SWST member

treated softwoods, emissions of volatile terpenes and hexanal are drastically decreased, whereas those of acetic acid and furfural increase. Similarly, in thermally treated hardwoods, the emissions of hexanal and pentanal are reduced, whereas acetic acid and furfural, as well as other compounds increase. In addition, formaldehyde emissions are ubiquitous, albeit at low concentrations, but increase following heat treatment. Furthermore, the number of VOCs emitted from thermally treated wood increases with heat treatment temperature. This review article will help guide future research, particularly the evaluation of the impact of different wood species on indoor air quality and the development of modification techniques that target extraction or suppression of VOC emissions.

Keywords: Wood, thermally modified wood, volatile organic compounds, VOCs, wood volatile organic compounds, WVOCs.

INTRODUCTION

Volatile organic compounds (VOCs) are a diverse group of compounds that are present in elevated concentrations in indoor air, generally exceeding the outdoor levels by several times. Indoor VOCs are emitted by a variety of human activities and sources, such as cleaning and personal care products, combustion sources such as cooking, smoking, heating, paints, adhesives, furniture, floorings, carpets, and building materials, including wood and wood-based composite materials (Wallace 1993). Total VOC concentrations are generally greatest in new buildings and then drop rapidly in the first 6 mo and gradually decline within a year (Brown 1999). VOC emissions have important contribution to indoor air quality because people spend more than 80% of their time in the indoor built environment and can significantly impact human well-being and health (Liu and Little 2012).

After the focus on formaldehyde as a major indoor pollutant, there has been considerable interest in VOCs as potential causes of adverse health effects (Wolkoff and Nielsen 2001). Anthropogenic VOCs (AVOCs) emitted, eg from the synthetic adhesive resins used in wood composites and their negative effects on humans have been well studied. The associated effects include irritation of mucosa (eyes, nose, and throat), allergies and asthma, discomfort, nausea, sick building syndrome, or cancer, such as nasopharyngeal carcinoma (Liu and Little 2012). On the other hand, biogenic VOCs (BVOCs) of natural origin are released by living organisms. However, the distinction between AVOCs and BVOCs is often not as clear-cut as is the case with formaldehyde, which originates from both

artificial and natural sources (Wallace 1993; Salthammer et al 2010). A well-known example of BVOCs are volatile terpenes, secondary metabolites emitted from plants having a biological function as volatile signaling molecules, and are released from forests into the atmosphere in large quantities where they have an impact on climate (Laothawornkitkul et al 2009).

Moreover, volatile terpenes—monoterpenes and sesquiterpenes—are stored in the resin canals of softwoods, eg in the resin ducts in pine species or resin blisters in fir species (Fall 1999; Wolpert 2012). These terpenes can be released from a standing tree, during processing or during use. By contrast, hardwoods do not have these storage compartments (Laothawornkitkul et al 2009) and typically do not contain and emit volatile terpenes (Fengel and Wegener 1989). Biologically active volatile terpenes from wood can elicit various positive or negative physiological responses in different organisms and have been shown to have potential beneficial effects on human well-being and health, such as relaxation or stress reduction, improvement in immune function, anticancer, anti-inflammatory, antioxidant, and antimicrobial activities, as well as others (Son et al 2013; Lee et al 2015; Ikei et al 2017).

In addition to volatile terpenes, a variety of other VOCs are emitted from untreated and thermally modified wood (Englund 1999; Manninen et al 2002). The term used to designate VOCs emitted from wood is, however, not consistent across the studies because various names have been used, such as “biogenic VOCs or BVOCs” (Fedele et al 2007), “natural VOCs or NVOCs” (Son et al 2013), “phytoncides” (Li et al 2009), and “wood VOCs” (Vainio-Kaila et al 2017). We have decided to

use the latter term throughout this article and suggest its use when collectively referring to any VOC that has been emitted from either untreated or thermally modified softwood or hardwood, although wood VOCs (sometimes abbreviated WVOCs), such as formaldehyde or volatile terpenes, can also be released from other sources like different materials or plants.

Wood VOC emissions can be divided into *primary* and *secondary VOC emissions*. Primary VOCs are free, nonbound volatile compounds, such as volatile terpenes, that are initially present in high concentrations in wood because of their biological function in trees (Gabriel et al 2015). On the other hand, secondary VOCs, including hexanal, pentanal, and acetic acid, are formed from chemically or physically bound compounds that are liberated by chemical (eg oxidation, hydrolysis) or physical (eg mechanical wear) degradation of wood or wood extractives (Wolkoff 1999; Culleré et al 2013; Gabriel et al 2015). These emissions depend on several boundary conditions or factors, such as temperature, the presence of oxidizing agents (oxygen and other radicals, ozone), (UV-) light, air velocity, moisture, humidity, maintenance, wear, wood species or type, and age (Salthammer et al 1998; Wolkoff 1998, 1999; Knudsen et al 1999; Wolkoff and Nielsen 2001; Gabriel et al 2015). Regarding the temporal aspect of both types of emissions, primary VOCs are at first emitted in large amounts and then drastically decrease and generally dominate for a period of up to several months or a year and then gradually decline, whereas significantly lower concentrations of secondary VOCs can be emitted continuously over a longer period of time (Wolkoff 1995, 1999; Knudsen et al 1999; Wolkoff and Nielsen 2001). In addition to solid materials such as wood, indoor chemistry can occur in air that results in the formation of secondary VOCs in indoor air, which are also relevant to human health (Salthammer et al 1998).

The emissions of VOCs from some softwood and hardwood species have been well-studied (Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000; Hyttinen et al 2010). However, VOC emissions from thermally modified wood,

which displays different emission profiles because of various thermochemical reactions occurring during the heat treatment, have not been investigated in as much detail (Manninen et al 2002; Mayes and Oksanen 2003; Peters et al 2008; Hyttinen et al 2010; Elaieb et al 2015; Xue et al 2016). To our knowledge, the studies on VOC emissions from (thermally modified) wood have not been consistently compiled, reviewed, and summarized.

Therefore, in this review article, we summarize the scientific literature on VOCs emitted from different species of untreated and thermally modified wood with the aim to give a general picture of the characteristics of softwood and hardwood emissions. In addition, the main groups of wood VOCs and their emission properties are presented, as well as the factors influencing these emissions are listed.

Thus, the comprehensive information gathered in this review article should support and enable further research on VOCs emitted from untreated and thermally modified wood and help evaluate the influence of different (thermally modified) wood species on indoor air quality and accordingly on human well-being and health. Furthermore, the article may aid in the development of thermal modification techniques steered toward target wood VOCs.

Literature Review Methods and Results

For this review article, peer-reviewed scientific articles, book chapters, and books, as well as conference proceedings published in English were selected on the topic of VOCs from untreated and thermally modified wood. Because the review focuses on solid wood and thermally treated wood, the studies involving VOCs from wood-based composites, wood-plastic composites, chemically modified wood, impregnated wood, surface-treated wood (finish coatings, lacquers, paints, etc.), as well as from other materials were not included. Moreover, formaldehyde emitted from solid wood was briefly described because there are numerous reviews

already published on this subject and the main focus of the review was other wood VOCs. Published standards related to VOCs from wood were included as well.

The selection of publications was based on searches of the Web of Science, Scopus, and Google Scholar databases. First, separate searches were performed using various combinations of keywords as search terms, such as “wood”, “thermally modified/treated wood”, “volatile organic compounds”, “VOCs”, “biogenic VOCs”, “BVOCs”, “natural VOCs”, “NVOCs”, “wood VOCs”, “phytoncides”, and “emission”. These returned numerous hits that were subsequently filtered by selecting the most relevant publications related to the topic. In addition, relevant publications cited in the selected references were also used, which resulted in a total of 84 reviewed publications (including standards).

VOC EMISSIONS FROM UNTREATED WOOD

Various groups and amounts of VOCs are emitted from wood depending on the type of wood, softwood or hardwood, and species. Wood VOC emissions are dominated by *volatile terpenes* (monoterpenes and sesquiterpenes), typically emitted only from softwoods, followed by *aldehydes* (hexanal, propanal, butanal, pentanal, heptanal, acetaldehyde, formaldehyde, and 2-furancarboxaldehyde (furfural)), *organic acids* (acetic acid, hexanoic acid, and formic acid), *alcohols* (ethanol and methanol), *ketones* (acetone or 2-propanone), *aliphatic and aromatic hydrocarbons*, *esters*, and *ethers*. Generally, softwoods emit significantly higher amounts of VOCs than hardwoods because of large amounts of volatile terpene emissions (Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000; Manninen et al 2002; Roffael 2006; Peters et al 2008; Hyttinen et al 2010). VOCs emitted from different species of wood are presented in Table 1.

Softwood Emissions

The highest concentrations of wood VOCs are released from softwoods because of volatile

terpene emissions, but they also emit significantly lower amounts of secondary emissions, such as aldehyde hexanal and acetic acid (Englund 1999; Mayes and Oksanen 2003; Hyttinen et al 2010). Of the well-studied softwood species, Scots pine (*Pinus sylvestris*) wood emits the highest concentrations of VOCs, predominantly monoterpenes, including α -pinene, Δ^3 -carene, β -pinene, D-limonene, camphene, β -phellandrene, and terpinolene (Englund 1999; Mayes and Oksanen 2003; Hyttinen et al 2010; Czajka and Fabisiak 2012). Scots pine is followed by Norway spruce (*Picea abies*), which emits monoterpenes, including α -pinene, D-limonene, β -pinene, and Δ^3 -carene (Englund 1999; Hyttinen et al 2010; Czajka and Fabisiak 2013). European larch (*Larix decidua*) releases less volatiles, followed by silver fir (*Abies alba*), which emits the least VOCs as a result of its specific wood anatomy which lacks resin canals (Czajka and Fabisiak 2014). Compared with other softwoods, European larch (Waliszewska et al 2013) and Japanese cedar or sugi (*Cryptomeria japonica*) (Ohira et al 2009; Matsubara and Kawai 2014; Matsubara et al 2017) emitted a wider spectrum of sesquiterpenes in addition to monoterpenes. In rough terms, pine wood emission rates were 100 times and spruce wood 30 times higher than hardwood emission rates (Risholm-Sundman et al 1998; Peters et al 2008). Other studies with pine recorded VOC emissions 4-20 times higher than spruce wood (Englund 1999; Larsen et al 2000; Jensen et al 2001; Hyttinen et al 2010; Gabriel et al 2015). Studies have shown that as high as 70-90% of total VOC emissions from softwood are volatile terpenes and only up to 25% are aldehydes and acetic acid (Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000; Manninen et al 2002; Roffael 2006; Hyttinen et al 2010). Aliphatic aldehydes such as hexane are mainly formed by oxidation of fatty acids produced by the hydrolysis of fats in wood. Because of the higher fat content in pine, emissions of aldehydes were found to be higher from pine than from spruce wood (Hyttinen et al 2010; Gabriel et al 2015).

Table 1. VOCs emitted from different species of untreated solid wood and thermally modified wood (wood species are grouped into three categories: softwoods, hardwoods, and tropical woods. The listed VOCs are generally ordered by decreasing concentration. Note that formaldehyde, acetaldehyde, formic acid, and methanol were not reliably detectable by the methods used and are, therefore, typically not listed although their occurrence cannot be excluded).

Wood species	VOCs emitted from untreated wood	VOCs emitted from thermally modified wood	Reference
Softwood species			
Cedar, Japanese or sugi (<i>Cryptomeria japonica</i>)	δ -Cadinene, α -muurolene, 4-epi-cubebol, cubebol, β -cadinene, β -caryophyllene, calarene, α -caryophyllene, 1,10-di-epi-cubanol, α -cubebene, α -elemene, β -cubebene, aromadendrene, thujopsene, and β -cedrene	ND	Ohira et al (2009) Matsubara and Kawai (2014) Matsubara et al (2017)
Fir, Douglas (<i>Pseudotsuga menziesii</i>)	α -Pinene, β -pinene, limonene, <i>p</i> -cymene, β -myrcene, 3-carene, 4-terpineol, α -terpinene, and α -terpineol	ND	Meyer and Boehme (1997) Milota and Lavery (1998) Lavery and Milota (2000) Waliszewska et al (2013)
Larch, European (<i>Larix decidua</i>)	Isolimonene, limonene, τ -elemene, neoisolongifolene, 8,9-dehydro-, β -pinene, humulene (α -caryophyllene), germacrene D, camphene, isolongifolene, longifolene, α -cubebene, 2-carene, τ -muurolene, and β -caryophyllene	ND	
Pine, Aleppo (<i>Pinus halepensis</i>)	β -Caryophyllene, hexanal, β -pinene, camphene, nonanal, isobomyl acetate, humulene (α -caryophyllene), β -caryophyllene oxide, and formaldehyde	Acetic acid, vanillin, guaiaiyacetone, β -pinene, terpinyl acetate, hexanoic acid (caproic acid), and furfural	Elaieb et al (2015)* Tasooji et al (2017)
Pine, maritime (<i>Pinus pinaster</i>)			Elaieb et al (2015)*
Pine, radiata (<i>Pinus radiata</i>)			Son et al (2013)
Pine, Japanese red (<i>Pinus densiflora</i>)	α -Pinene, limonene, β -pinene, camphene, <i>p</i> -cymene, α -terpinene, and 3-carene	ND	Son et al (2013)
Pine, Korean (<i>Pinus koraiensis</i>)	α -Pinene, β -pinene, limonene, camphene, <i>p</i> -cymene, and α -terpinene	ND	Son et al (2013)

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Table 1. Continued.

Wood species	VOCs emitted from untreated wood	VOCs emitted from thermally modified wood	Reference
Pine, Scots (<i>Pinus sylvestris</i>)	<p>α-Pinene, 3-carene, limonene, β-pinene, acetone, hexanal, nonanal, β-myrcene, β-phellandrene, terpinolene, isoterpinolene, camphene, pentalan, acetaldehyde, propanal, butanal, acetic acid, hexanoic acid, furfural, ketone 6-methyl-5-hepten-2-one, and formaldehyde</p>	<p>Furfural, acetic acid, acetone (2-propanone), methyl ester of acetic acid, 1-OH-2-propanone, limonene, ethanol α-pinene, 3-carene, camphene, and hexanal</p>	<p>Meyer and Boehme (1997) Risholm-Sundman et al (1998) Englund (1999) Englund and Nussbaum (2000) Larsen et al (2000) Jensen et al (2001) Manninen et al (2002)* Mayes and Oksanen (2003)* Hyttinen et al (2010)* Böhm et al (2012) Wang et al (2018)*</p>
Pine, southern yellow (<i>Pinus</i> spp.)	<p>α-Pinene (2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene), β-pinene, α-terpineol (<i>p</i>-menth-1-en-8-ol), 1-methoxy-4-(2-propenyl)-benzene (estragole), limonene (1-methyl-4-(1-methylethenyl)-(s)-cyclohexene), and 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane (camphene)</p>	<p>Furfural (2-furancarboxaldehyde), α-pinene (2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene), tridecane, limonene (1-methyl-4-(1-methylethenyl)-(s)-cyclohexene), nonanal, 1-methoxy-4-(2-propenyl)-benzene (estragole), dodecane, <i>o</i>-cymene (methyl(1-methylethyl)-benzene), benzaldehyde, fenchyl acetate (1,3,3-trimethylbicyclo[2.2.1]hept-2-yl acetate), acetic acid, heptadecane, and α-terpineol (<i>p</i>-menth-1-en-8-ol)</p>	

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Table 1. Continued.

Wood species	VOCs emitted from untreated wood	VOCs emitted from thermally modified wood	Reference
Spruce, Norway (<i>Picea abies</i>)	α-Pinene, limonene, β-pinene, 3-carene, acetone, hexanal, α-terpineol, sylvestrene, β-caryophyllene, γ-cadinene, δ-cadinene, β-phellandrene, β-myrcene, pentanal, furfural, acetaldehyde, acetic acid, hexanoic acid, nonanal, toluene, butanol, and formaldehyde	Acetic acid, furfural, 5-methylfurfural, α-pinene, limonene, and hexanal	Meyer and Boehme (1997) Risholm-Sundman et al (1998) Englund (1999) Englund and Nussbaum (2000) Larsen et al (2000) Jensen et al (2001) Peters et al (2008)* Steckel et al (2010) Hytinen et al (2010)* Böhm et al (2012) Czajka and Fabisiak (2013)
Hardwood species Ash, European (<i>Fraxinus excelsior</i>)	Acetaldehyde, methanol, propanal, formaldehyde, butanal, 2-pentylfuran, acetic acid, hexanal, furfural, and terpenes	Acetic acid, furfural, 5-methylfurfural, and hexanal	Risholm-Sundman et al (1998) Larsen et al (2000) Jensen et al (2001) Peters et al (2008)* Hytinen et al (2010)*
Aspen, European (<i>Populus tremula</i>)	Hexanal, acetic acid, pentanal, 1-pentanol, 1-penten-3-ol, 1-hexanol, and hexanoic acid	Acetic acid, furfural, and propanoic acid	Hytinen et al (2010)*

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Table 1. Continued.

Wood species	VOCs emitted from untreated wood	VOCs emitted from thermally modified wood	Reference
Beech, European (<i>Fagus sylvatica</i>)	Hexanal, ethanol, acetaldehyde, 2-pentylfuran, methanol, acetone, hexanoic acid, acetic acid, propanal, butanal, pentanal, furfural, and formaldehyde	Acetic acid, furfural, 5-methylfurfural, and hexanal	Meyer and Boehme (1997) Risholm-Sundman et al (1998) Englund (1999) Larsen et al (2000) Jensen et al (2001) Peters et al (2008)* Böhm et al (2012) Risholm-Sundman et al (1998) Englund (1999) Böhm et al (2012)
Birch, downy (<i>Betula pubescens</i>)	Hexanal, pentanal, acetone, 2-pentylfuran, terpene, methanol, and acetic acid	ND	
Birch, silver (<i>Betula pendula</i> or <i>Betula verrucosa</i>)	Hexanal, pentanal, hexanoic acid, acetic acid, ethanol, and formaldehyde	ND	
Cherry, black (<i>Prunus serotina</i>)	Acetic acid, 2-pentylfuran, methanol, and hexanal	ND	
Maple, sugar (<i>Acer saccharum</i>)	Methanol, 2-pentylfuran, hexanal, and acetic acid	ND	
Maple, sycamore (<i>Acer pseudoplatanus</i>)	Acetic acid, hexanal, pentanal, and furfural	Acetic acid, furfural, 5-methylfurfural, and hexanal	Peters et al (2008)*
Oak, Australian silky (<i>Grevillea robusta</i>)	Ethanol, hexanal, (<i>E</i>)-2-hexenal, (<i>Z</i>)-3-hexen-1-ol, acetaldehyde, and acetone	ND	Fedele et al (2007)
Oak, common (<i>Quercus robur</i>)	Acetic acid, methanol, furfural, hexanoic acid, acetone, acetaldehyde, propanal, butanal, 2-pentylfuran, hexanal, ethanol, and formaldehyde	ND	Meyer and Boehme (1997) Risholm-Sundman et al (1998) Englund (1999) Larsen et al (2000) Jensen et al (2001) Böhm et al (2012) Liu et al (2018)
Poplar, Cathay or Manchurian (<i>Populus cathayana</i>)	Acetic acid, hexanoic acid, tetradecane, hexanal, benzene, 1-dodecanol, tridecane, pentadecane, (<i>Z</i>)-2-decenal, ethanol, nonanal, and dodecanal	ND	

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Table 1. Continued.

Wood species	VOCs emitted from untreated wood	VOCs emitted from thermally modified wood	Reference
Poplar, Chinese white (<i>Populus tomentosa</i>) sapwood	Oxalic acid, methylnaphthalene, capraldehyde (decanal), 2-nonenal, naphthalene, nonanal, and hexadecane	2-Nonenal, phenol, furfural (furfuraldehyde), decanal, methylnaphthalene, and methyl benzoate phenol and furfural	Xue et al (2016)*
Poplar, white (<i>Populus alba</i>)	ND		Čech and Tesarová (2015)*
Tropical wood species			
Meranti, pink (<i>Shorea</i> sp.)	α -Cubebene, β -caryophyllene, τ -elemene, isolongifolene, neoisolongifolene, and α -pinene,	ND	Waliszewska et al (2013)
Merbau (<i>Intsia</i> sp.)	Hexanal, pentanal, and acetone	ND	Stachowiak-Wencek and Prądzynski (2014)
Rubber tree (<i>Hevea brasiliensis</i>)	Acetic acid, tetradecane, 1-dodecanol, benzene, pentadecane, 2,4-di- <i>tert</i> -butylphenol, tridecane, 2-pentylfuran, 2-propylfuran, and methanol	ND	Risholm-Sundman et al (1998)
Teak (<i>Tectona</i> sp.)	Acetone and hexanal	ND	Liu et al (2018) Stachowiak-Wencek and Prądzynski (2014)
Wenge (<i>Milletia laurentii</i>)	Pentanal, acetone, hexanal, furfural, and 2-pentylfuran	ND	Stachowiak-Wencek and Prądzynski (2014)
Zebrawood (<i>Microberlinia brazzavillensis</i>)	Pentanal, acetone, hexanal, 2-pentylfuran, and furfural	ND	Stachowiak-Wencek and Prądzynski (2014)

ND, not determined; VOCs, volatile organic compounds.

* These references cover both modified and unmodified wood. All other references cover unmodified wood only.

After the initially high levels of total VOCs or volatile terpene emissions from Scots pine and Norway spruce, they decrease considerably with drying and over time—roughly 50% in 2 wk (Englund 1999; Roffael 2006; Hyttinen et al 2010; Czajka and Fabisiak 2012, 2013). Furthermore, emission rates decreased to a greater degree in spruce than in pine (Englund 1999; Hyttinen et al 2010; Czajka and Fabisiak 2012, 2013), which may be related to the irreversible aspiration of pores that occurs when spruce is dried below the FSP (Englund 1999).

Heartwood has been shown to emit larger amounts of VOCs than sapwood because of higher emission rates of volatile terpenes, as shown for Scots pine (Englund 1999; Czajka and Fabisiak 2012; Vainio-Kaila et al 2017), Norway spruce (Vainio-Kaila et al 2017), and silver fir (Czajka and Fabisiak 2014). Pine heartwood, eg contained about 5-15 times the amount of volatile terpenes (and higher relative emissions of monoterpene 3-carene) found in sapwood (Englund 1999; Ingram et al 2000; Czajka and Fabisiak 2012; Vainio-Kaila et al 2017) as it produces larger amount of resin and extractives (FPL 1966; Panda 2008). Scots pine (Englund 1999; Czajka and Fabisiak 2012; Vainio-Kaila et al 2017), Norway spruce (Vainio-Kaila et al 2017), and silver fir (Czajka and Fabisiak 2014) sapwoods have been shown to emit higher emissions of aldehydes (hexanal) and carboxylic acids (acetic acid) relative to heartwood. This is due to the fact that fats (which are hydrolyzed to fatty acids that are oxidized to aldehydes) occur mainly in sapwood (Gabriel et al 2015), and the acetyl content (acetyl groups are hydrolyzed and cleaved to acetic acid) is higher in sapwood than in heartwood (Maga 1988). Similarly, total VOC emissions from mature wood were higher (by approximately 2.7 times) compared with those from juvenile wood in Norway spruce, again predominantly due to higher volatile terpene emissions (Czajka and Fabisiak 2013). Moreover, the amount of VOCs, specifically monoterpenes, was highest in stem wood, whereas lower amounts were found in branch wood (Wolpert 2012). Knots and pitch pockets in wood may also

contribute to higher emission rates, acting as sources of volatile terpenes as was found in spruce (Englund 1999) and pine, where knots contained about 10 times the amount of volatile terpenes found in sapwood (Ingram et al 2000). In addition, injured wood regions, caused by herbivore predators and parasites, microorganisms, lightning, wind, lumbering activity, etc., accumulate large amounts of volatile terpene-containing resin, also resulting in higher emissions of VOCs (Trapp and Croteau 2001; Wolpert 2012).

Hardwood Emissions

VOC emissions from hardwoods are substantially lower than that of softwoods because they do not contain and emit volatile terpenes. Generally, hardwoods contain higher nonvolatile terpenes, other than in some tropical species where monoterpenes and sesquiterpenes can also be found (Fengel and Wegener 1989), eg in the tropical species pink meranti (*Shorea* sp.) that emitted greater amounts of sesquiterpenes, followed by monoterpenes (Waliszewska et al 2013).

Instead, hardwoods emit a wider variety of carbonyl compounds (aldehydes, carboxylic acids, and ketones) and alcohols, mainly the aldehydes hexanal and pentanal, as well as acetic acid. Emission of acetic acid is generally greater from hardwoods than softwoods because of the higher amount of acetyl groups in hardwood hemicelluloses (Fengel and Wegener 1989; Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000; Roffael 2006; Peters et al 2008; Hyttinen et al 2010). Hexanal is the dominant emission from European beech (*Fagus sylvatica*), silver birch (*Betula pendula* or *Betula verrucosa*) and downy birch (*Betula pubescens*) (Risholm-Sundman et al 1998; Englund 1999), and European aspen (*Populus tremula*) (Hyttinen et al 2010). By contrast, common oak (*Quercus robur*) and black cherry (*Prunus serotina*) exhibit the lowest total VOC emission rates, dominated by acetic acid, followed by methanol and 2-pentylfuran, as well as acetone, acetaldehyde, and

propanal, but do not emit appreciable amounts of hexanal (Risholm-Sundman et al 1998; Englund 1999). European ash (*Fraxinus excelsior*) and sugar maple (*Acer saccharum*) have shown similar emission profiles (Risholm-Sundman et al 1998; Larsen et al 2000). Aldehydes are less present in emissions from poplar wood, which predominantly emits carboxylic acids; Chinese white poplar (*Populus tomentosa*) sapwood emits oxalic acid (Xue et al 2016) and Cathay or Manchurian poplar (*Populus cathayana*) emits acetic and hexanoic acids (Liu et al 2018).

However, considerable variability in VOC emissions has been observed, even between different samples of the same wood species (Englund 1999). The factors that influence emissions are reviewed in Section 4 and Table 2. Especially in softwoods, pine in particular, followed by spruce, the amount and composition of VOC emissions or volatile terpenes have been observed with large variations with significant differences in emission rates of α -pinene and 3-carene (Englund 1999; Larsen et al 2000). Small variations in the amount of heartwood or knots in a wood sample have been observed to result in large changes in VOC emissions (Ingram et al 2000).

Groups of Wood VOCs

Volatile terpenes and terpenoids. Volatile terpenes are monoterpenes and sesquiterpenes containing 10 or 15 carbons, respectively, that have low boiling points/high vapor pressures. Diterpenes (C_{20}) and higher terpenes are volatile at higher temperatures. Terpenes are hydrocarbon compounds derived from and composed of isoprene (C_5) units, whereas terpenoids include additional (oxygen-containing) functional groups. These compounds are the constituents of plant essential oils and conifer resins, with many being fragrant and give an intense, pleasant odor (Fengel and Wegener 1989; Risholm-Sundman et al 1998; Salthammer 2004).

Resin-rich softwoods, such as pine and spruce, emit very high concentrations of monoterpenes

and a monoterpene, as well as a variety of sesquiterpenes and sesquiterpenoids (Table 1). Volatile terpenes are not homogeneously distributed within softwoods but are stored in discrete resin canals that create terpene-rich sections of the material (Wolpert 2012). This may explain intraindividual variability of volatile terpene emissions from softwoods, whereas large interindividual differences have been attributed more to genetic factors than to growth conditions (Englund 1999; Larsen et al 2000).

By contrast, hardwoods generally do not emit volatile terpenes but contain higher terpenes, which are nonvolatile at ambient conditions and thus not released (Fengel and Wegener 1989).

Aldehydes. Aldehydes are some of the most undesirable indoor VOCs because of their unpleasant odor and potential toxicity (Salthammer 2004; Liu and Little 2012). Several aldehydes are emitted from wood in relatively low concentrations (Table 1). Of these, hexanal emissions are largest and are almost ubiquitous in both hardwoods and softwoods, whereas minor amounts of pentanal, nonanal, heptanal, octanal, acetaldehyde, furfural, and formaldehyde are emitted from different wood species (Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000; Manninen et al 2002; Roffael 2006; Hyttinen et al 2010; Gabriel et al 2015). Aldehydes, such as saturated aliphatic aldehydes, are degradation products of wood formed mainly by oxidation and scission of unsaturated fatty acids (autoxidation) produced by the hydrolysis of fats in wood, which is accelerated at high temperatures (Gabriel et al 2015). Furfural appears in low concentrations as the main thermal degradation product of polysaccharides (hemicellulose and cellulose) at high temperatures (Risholm-Sundman et al 1998; Englund 1999; Hyttinen et al 2010; Stachowiak-Wencek and Prądyński 2014).

Formaldehyde is an important VOC because of its ubiquity in indoor air and the negative impact it has on human health (Liu and Little 2012). Of a variety of formaldehyde sources, those commonly related to wood are formaldehyde-based

Table 2. Endogenous and exogenous factors influencing VOC emissions from wood and thermally modified wood that should be considered and described when testing wood samples.

Factor	Influence	Reference
Endogenous Factors		
Tree/wood data		
Tree/wood species	Genetic factors – different wood species emit different types and concentrations of wood VOCs; substantial differences observed between softwoods and hardwoods	Risholm-Sundman et al (1998) Englund (1999) Larsen et al (2000)
Growth location (habitat)	Emissions are influenced by macro- and microclimate at the growth site, nutrient supply, and other growth conditions	Englund (1999) Granström (2005)
Date and time of harvesting	Wood experiences seasonal changes in chemical composition and content; time from harvesting to VOC analysis decreases emissions because of wood ageing	Englund (1999) Granström (2005) Gabriel et al (2015)
Type of wood sample/distribution of VOCs within the sample		
Heartwood/sapwood ratio	In softwoods, heartwood shows higher VOC emission rates than sapwood because of volatile terpenes, whereas sapwood emits higher concentration of aldehydes and carboxylic acids	Englund (1999) Larsen et al (2000) Czajka and Fabisiak (2012, 2014) Vainio-Kaila et al (2017) Czajka and Fabisiak (2013)
Mature/juvenile wood ratio	The mature zone shows higher VOC emission rates than juvenile zone	Wolpert (2012)
Stem/branch wood ratio	Higher concentrations of monoterpenes are emitted from stem compared with branch wood	Wolpert (2012)
Presence of resin canals/ducts	Volatile terpenes are not homogeneously distributed within softwood, which contains discrete terpene-rich wood spots such as resin canals or ducts that emit higher VOC concentrations	Wolpert (2012)
Portion of knots, pitch pockets, or other defect area	Knots, pitch pockets, and other defects may influence VOC emissions by increasing volatile terpene concentration in softwoods	Englund (1999) Ingram et al (2000)
Presence of tree/wood injuries	Volatile terpene-containing resin is accumulated in large amounts in the injured wood regions resulting in higher VOC emissions	Trapp and Croteau (2001) Wolpert (2012)
Exogenous factors		
Wood sample storage		
Storage method (packaging)	Wood samples should be properly stored (packed) according to ISO 16000-11 and protected from chemical contamination or any physical exposure (eg heat, light, and humidity)	ISO 16000-11 (2006) Roffael (2006) Čech and Tesařová 2015
Storage time	VOC emission (predominantly volatile terpenes) rates decrease with storage time because of ageing of the sample; therefore, it is recommended to minimize the storage time	Salthammer 2004 ISO 16000-11 (2006) Roffael (2006) Čech and Tesařová (2015) Gabriel et al (2015)
Storage temperature	During storage, temperature seems to be more important in decreasing the emissions than the storage time	Gabriel et al (2015)
Wood treatment		
Drying or thermal treatment	Drying and thermal treatment influence—decrease (softwoods) or increase (hardwoods) VOC emissions; formaldehyde emissions were higher in dry wood than in the green wood	Meyer and Boehme (1997) Englund (1999) Peters et al (2008)

Continued on next page

Table 2. Continued.

Factor	Influence	Reference
Surface treatment and finish coatings	Generally, surface treatment drastically reduces wood VOC emissions; however, lacquers and paints may contribute with their own VOCs from solvents and other agents, and thus can increase VOC emission rates; oils, waxes, and waterborne lacquer contain solvents, but also allow VOCs to be emitted from wood	Risholm-Sundman et al (1998) Englund (1999) Larsen et al (2000) Čech and Tesařová (2015)
Wood planing	Planing increases VOC emission rates; therefore, time period between planing and the analysis is important	Risholm-Sundman et al (1998)
Emission test chamber conditions		
Temperature (23 ± 2°C)	Higher temperatures increase emission of wood VOCs—individual VOCs are emitted at certain temperatures depending on their volatility, boiling point, or vapor pressure, as well as on its diffusion coefficient, etc. Moreover, with temperature, the formation of secondary emissions, such as hexanal and pentanal, is increased	Englund (1999) Salthammer (2004) ISO 16000-9 (2006) Gabriel et al (2015)
Wood MC and RH (50 ± 5%)	Reduced MC of wood below 10% elevates VOC emissions by increasing the temperature (because of decreased evaporative cooling) and facilitating wood degradation (leading to the formation of VOCs, such as aldehydes and methanol). Wet wood is generally less susceptible to oxidation compared with dry wood, resulting in less secondary VOC emissions. However, at higher moisture contents, greater total VOC emissions were observed, resulting in more formaldehyde than in dry specimens	Milota and Wu (1997) Englund (1999) Su et al (1999) Granström (2005) ISO 16000-9 (2006) Gabriel et al (2015) Tasooji et al (2017) Vainio-Kaila et al (2017)
Presence of oxidizing agents	The formation of secondary VOCs and their emission depends on the presence of oxidizing agents (oxygen and other radicals, ozone) responsible for the oxidation of wood components (eg fatty acids that form aldehydes hexanal and pentanal)	Gabriel et al (2015)

adhesive resins frequently used in wood-based composites (Roffael 2006; Liu and Little 2012). Formaldehyde may form in indoor air by chemical reactions such as the oxidation of unsaturated VOCs (eg terpenes, such as α -pinene, β -pinene, and limonene) (Wolkoff 1995; Wolkoff et al 1997; Roffael 2006), as well as form naturally in solid wood from which it is released in minute, but still detectable amounts under normal ambient conditions (Larsen et al 2000; Roffael 2006). The European Standard EN 13986 (2005) for wood-based panel use in construction established formaldehyde emission classification system based on product type that classifies them into one of two emission classes—E1 or E2. It defines a

formaldehyde release limit of $3.5 \text{ m}\cdot\text{g}/\text{m}^2\cdot\text{h}$ for emission class E1 and $8 \text{ m}\cdot\text{g}/\text{m}^2\cdot\text{h}$ for emission class E2, using the EN 717-2 test method (EN 13986 2005).

In wood, biogenic formaldehyde is formed as a decomposition product of lignin, which have a higher emission potential than the main polysaccharide wood components hemicelluloses and cellulose, whereas formaldehyde emission from the extractives depends highly on their chemical composition (Schäfer and Roffael 2000; Wan and Frazier 2017). A study on hybrid poplar (*Populus nigra* \times *Populus maximowiczii*), European beech, silver birch, common oak, Scots

pine, and Norway spruce has shown the highest formaldehyde emission for beech (6.8 ppb) and the lowest for birch (3.6 ppb), and the emissions decreased after 2 wk of measurement (Böhm et al 2012). By contrast, Meyer and Boehme (1997) reported the highest formaldehyde emissions for oak (9 ppb) and the lowest for beech (2 ppb), whereas the emissions from pine, spruce, and Douglas-fir (*Pseudotsuga menziesii*) were in between. Moreover, it has been observed that in general, formaldehyde emissions were higher in dry wood than in the green wood. A study on Virginia pine (*Pinus virginiana*), yellow poplar (*Liriodendron tulipifera*), and radiata pine (*Pinus radiata*) has shown significant variations in the generation of formaldehyde within and between species of wood. Heating wood increased formaldehyde levels 3-60 times, depending on species, tissue type, and MC. Furthermore, heating with high moisture levels produced more formaldehyde than from dry specimens. Radiata pine generated the highest levels of formaldehyde when heated, far exceeding the other species studied (Tasooji et al 2017). In another study, it was shown that formaldehyde emissions from pine wood chips before processing (ie cutting) were 25% lower than the emission from wood particles after processing, which was 4.6% of the emission permitted for E1-class products (Boruszewski et al 2011).

Thus, it has been shown that the emission of formaldehyde depends on various exogenic (temperature, RH, air exchange level, and storage time) and endogenic (wood species, tissue type, and MC) factors and increases with thermal treatment during wood processing, including drying, pressing, and thermal hydrolysis. This may explain the observed variability in formaldehyde emission rates in studies on solid wood; nevertheless, the results are generally comparable (Roffael 2006; Salem and Böhm 2013; Wan and Frazier 2017).

Formaldehyde is a highly volatile compound and, thus, cannot be analyzed by commonly applied sampling methods for VOCs using Tenax adsorbents. Therefore, it is frequently disregarded in VOC emission studies (Englund 1999). Hence,

other analytical techniques for the detection of formaldehyde are used to determine its emission (Salthammer et al 2010) involving different standard sampling (ISO 16000-2, ISO 16000-3, and ISO 16000-4) and emission testing methods:

1. The chamber method (EN 717-1, ISO 12460-1, ISO 12460-2, ISO 16000-9, ASTM D6007, and ASTM E1333).
2. Gas analysis method (EN 717-2, ISO 12460-3).
3. Flask method (EN 717-3).
4. Perforator method (EN 120 and ISO 12460-5).
5. Desiccator method (ISO 12460-4, JIS A 1460, JAS 233, and ASTM D5582).
6. The National Institute of Occupational Safety and Health test method 3500 (1994) (Salthammer et al 2010; Salem and Böhm 2013).

Some of these standardized methods are also applicable for other VOCs emitted from building products, including wood and wood-based panels, which were largely summarized in the European Standard EN 16516 (2017) for construction products (EN 16516 2017). In addition, the ISO 16000-10 and ISO 16000-25 standards for emission test cell and microchamber methods, respectively, can be used to determine VOC emissions.

Organic acids. Carboxylic acids, predominantly acetic, hexanoic, and formic acid, are emitted in relatively low concentrations from wood, whereas other acids appear sparingly. Acetic and hexanoic acid are found in wood ubiquitously, whereas formic acid is highly volatile and cannot be collected and analyzed using Tenax sampling adsorbent; therefore, its occurrence frequently cannot be excluded (Englund 1999). Hardwoods, especially oak, followed by cherry, emit considerably higher emissions of acetic acid compared with softwoods (acetic acid is easily detectable by smelling fresh oak) (Risholm-Sundman et al 1998; Englund 1999). This is because acetic acid is formed by the hydrolysis and cleavage of acetyl groups (deacetylation) in lignin and hemicelluloses, and the amount of acetyl groups is higher in hardwood than in softwood (Risholm-Sundman et al 1998; Englund 1999; Peters et al

2008; Hyttinen et al 2010). On the other hand, hexanoic acid can be a result of further oxidation of hexanal (Englund 1999).

Acetic acid emitted from wood has been demonstrated to have deteriorating effect on museum artifact materials by causing metal corrosion and pigment discoloration. The effects varied greatly between wood species and were greater for the species western red cedar (*Thuja plicata*) and spruce that emit higher concentrations of VOCs, such as acetic acid and hinokitiol (Oikawa et al 2005).

Other wood VOCs. Methanol was found to be an important emission from different species of wood, mainly hardwoods, such as ash, beech, sugar maple, downy birch, oak, cherry, and rubber tree (*Hevea brasiliensis*) in a study using headspace gas chromatography coupled to mass spectrometry (Risholm-Sundman et al 1998). Ethanol emissions have been observed in beech and in smaller quantities in oak and silver birch, all in the green state (Englund 1999).

Emissions of ketones, such as acetone, have been found from birch, pine, spruce, beech, and oak (Risholm-Sundman et al 1998; Englund 1999; Larsen et al 2000). Although detectable, acetone is not easily quantified by sampling methods using a Tenax adsorbent because of the low breakthrough volume on the adsorbent tubes (Englund 1999; Hyttinen et al 2010). Other ketones have been observed from wood only in low quantities, such as 6-methyl-5-hepten-2-one from Scots pine (Manninen et al 2002).

Alkylfurans, such as ethyl-, propyl- and pentyl-furans, have been found in low concentrations in the emissions from most hardwoods. However, they are most likely formed during the analysis at an elevated temperature or due to high-temperature drying because furan and its derivatives are found among the thermal degradation products of cellulose and other polysaccharides (Risholm-Sundman et al 1998; Englund 1999; Stachowiak-Wencek and Prądzynski 2014).

It is important to note that the vast majority of the reviewed studies in this article (except for

Risholm-Sundman et al (1998) and Larsen et al (2000)) used sampling methods using Tenax adsorbents that are unsuitable for analysis of some highly volatile or reactive compounds, including formaldehyde, acetaldehyde, formic acid, and methanol. These compounds have, thus, not been detected; however, their occurrence cannot be excluded. Propanal and acetone are borderline cases that can be analyzed but have very low breakthrough volumes on these adsorbent tubes and, thus, are not easily quantified (Englund 1999). Therefore, different methods are used to analyze these compounds, such as headspace gas chromatography coupled to mass spectrometry (Risholm-Sundman et al 1998; Larsen et al 2000) or others (Salthammer et al 2010).

VOC EMISSIONS FROM THERMALLY MODIFIED WOOD

Wood modification is a process used to improve the material properties of wood by enhancing its dimensional stability, to reduce water sorption, to improve weathering performance and its decay resistance to extend its service life, etc. (Hill 2006). Thermal modification processes carried out at elevated temperatures are used to produce wood products for both exterior and interior applications because no chemicals are used in the treatment process (Militz and Altgen 2014).

During heat treatment, wood constituents are degraded leading to chemical changes, which result in altered physical and biological properties of thermally modified wood (Hill 2006), including changed VOC emissions (Table 1) (Manninen et al 2002; Mayes and Oksanen 2003; Peters et al 2008; Hyttinen et al 2010; Čech and Tesařová 2015; Elaieb et al 2015; Xue et al 2016). These heat-induced changes depend on the wood species (the most notable differences are between hardwoods and softwoods; Hill 2006; Militz and Altgen 2014). The conditions and steps of the treatment process, such as temperature, duration of the treatment, the initial MC of the wood, oxygen level, the heat transferring medium, pressure regime, etc., contribute to differences in properties as well (Hill 2006; Militz and Altgen 2014). The pressure

regime depends on the reactor system used (open or closed) resulting in different pressure levels, ranging from subatmospheric (vacuum), atmospheric, to elevated pressure environments (Hill 2006; Militz and Altgen 2014; Wentzel et al 2018, 2019a, 2019b). During thermal modification processes operated in open reactor systems at atmospheric pressures, volatile compounds are released from the treated wood and reactor (Mayes and Oksanen 2003; Militz and Altgen 2014). The removal of VOCs is even more pronounced in processes at subatmospheric pressures in vacuum conditions (Allegretti et al 2012; Hofmann et al 2013). On the other hand, in thermal modification processes at elevated pressure in closed reactor systems, VOCs are retained and accumulated (Stamm 1956; Poncsak et al 2009).

Thermochemical reactions occurring during the heat treatment of wood, including oxidation, dehydration, decarboxylation, transglycosylation, cross-linking, depolymerization of hemicelluloses by hydrolysis, and ramification of lignin, lead to thermal degradation of wood cell wall components and extractives, which changes their chemical composition (Kocaefe et al 2008; Esteves and Pereira 2009; Poncsak et al 2009). Temperatures above 150°C alter the physical and chemical properties of wood permanently (Akgül et al 2007) and chemical changes of wood components lead to new products and by-products, including VOCs that can be emitted from wood after the treatment. Most of the new (by-)products resulting from the degradation of wood polymers appear only above 200°C and are formed at treatment temperatures of 220°C and 230°C (Esteves and Pereira 2009; Poncsak et al 2009; Culleré et al 2013; Wang et al 2018). For example, decomposition temperature of hemicelluloses and cellulose are about 200 to 260°C and 240 to 350°C, respectively (Mayes and Oksanen 2003). Moreover, because of the extensive heat, moisture and VOCs, including volatile terpenes and other low-molecular weight compounds, evaporate from wood during the heat treatment (Manninen et al 2002; Poncsak et al 2009). Volatiles start to migrate out of the wood at low temperatures (under 130°C), whereas the

major part of the extractives leave wood under 200°C, and at 200°C, most of the volatiles are already removed (Poncsak et al 2009).

Heat treatment causes a variety of changes in VOC emissions from thermally modified wood compared with untreated wood. Changes include VOC quantity and quality, such as changes in total VOC emissions, in emitted VOCs, as well as newly formed VOCs not present in untreated wood. The resulting VOCs emitted from different species of thermally modified wood compared with the untreated counterparts are presented in Table 1.

Changes in Total VOC Emissions

In general, the total VOC emission from thermally treated softwood decreases (Manninen et al 2002; Mayes and Oksanen 2003; Peters et al 2008; Hyttinen et al 2010; Elaieb et al 2015), whereas from thermally treated hardwood, it increases after the heat treatment compared with the untreated wood (Peters et al 2008; Čech and Tesařová 2015; Xue et al 2016).

Total VOC emissions from thermally modified softwoods decreased as treatment temperature rose in Scots pine. The decrease compared with the air-dried counterpart was about $1.8 \times$ (at 180°C for 4 h) or $6.3 \times$ (at 230°C for 4 h) (Mayes and Oksanen 2003); $8 \times$ (at 230°C for 24 h) (Manninen et al 2002); or $27.8 \times$ (at 212°C for 2 to 3 h) (Hyttinen et al 2010). Aleppo pine (*Pinus halepensis*), radiata pine, and maritime pine (*Pinus pinaster*) all showed similar behavior and a large decrease in total VOC emissions after thermal treatment. This was presumably due to severe conditions over a longer treatment period that was performed under vacuum atmosphere—initial drying at 103°C for 48 h and three-step heat treatment with a 15-h duration and setpoints at 103°C, 170°C, and 230°C (Elaieb et al 2015). However, in heat-treated Norway spruce, the decrease was slightly lower, approximately $1.7 \times$ (at 180°C) or $2.3 \times$ (at 200°C) (Peters et al 2008); or $3.9 \times$ (190°C for 2 to 3 h) (Hyttinen et al 2010). This may be because the untreated spruce

wood contains lower levels of volatile terpenes than pine and because lower temperatures were used in the heat treatment. As concluded from these studies, in softwood, the decrease in total VOC emissions after heat treatment depends on the temperature and duration of the process, as well as on the pressure regime. The higher the temperature and the longer the treatment, the more volatile the terpenes are removed, especially in vacuum conditions, resulting in lower VOC emissions from thermally treated softwood. Moreover, the decrease also depends on the softwood species—those with higher volatile terpene amounts, ie pine, show greater decrease after the heat treatment.

By contrast, thermally treated hardwoods tend to emit greater total quantities of VOC emissions than untreated wood (Peters et al 2008; Čech and Tesařová 2015; Xue et al 2016). Emissions have been observed to increase with treatment temperature. For beech specimens, an increase of $2.8 \times$ (at 180°C) or $4 \times$ (at 200°C) was reported (Peters et al 2008); and for white poplar (*Populus alba*), the increase was $2.4 \times$ at 180°C and $5.7 \times$ at 200°C (Čech and Tesařová 2015). In some thermally modified hardwood species, VOC emissions were the highest after moderate temperature treatments (eg 180°C). After more severe treatments using higher temperatures (eg 200°C or 220°C), the increase was lowered. This was noted for ash ($3.4 \times$ at 180°C or $1.7 \times$ at 200°C) and sycamore maple (*Acer pseudoplatanus*) ($5.7 \times$ at 180°C or $4.9 \times$ at 200°C) (Peters et al 2008). A similar pattern was observed for Chinese white poplar sapwood (Xue et al 2016). However, in European aspen, a $4.7 \times$ decrease was observed in total VOC emissions after heat treatment at 190°C for 2 to 3 h (Hytinen et al 2010).

The difference in changes in the total contents of VOC emission between thermally treated softwood and hardwood, which either decrease or increase in comparison with untreated wood, respectively, is presumably because softwoods contain high concentration of volatile terpenes. These are initially present in untreated softwoods and are released as primary emissions, which is

facilitated at high temperatures during heat treatment resulting in lower emissions from the heat-treated softwood. Conversely, hardwoods generally do not contain volatile terpenes but emit secondary VOCs formed in wood degradation processes, which is accelerated at elevated temperature, therefore, are increasingly produced during the heat treatment and released afterward.

Furthermore, variability was observed in total VOC emissions from thermally modified wood between different studies, which is presumably attributable to general factors influencing VOC emissions from wood (see Section 4), as well as due to the variety of thermal treatment processes used.

Changes in Emitted VOCs

In thermally treated wood, there is generally an increase in the emissions of carboxylic acids and their esters (predominantly acetic acid, which is one of the major components formed by thermal treatment), as well as an increase in aldehydes (mainly furfural and 5-methylfurfural), ketones (acetone), alcohols, and aliphatic and aromatic hydrocarbons, some of which are new products formed during heat treatment. Volatile terpenes (from softwoods), and the aldehydes hexanal and pentanal significantly decrease after the heat treatment compared with the untreated wood (see Table 1) (Manninen et al 2002; Mayes and Oksanen 2003; Peters et al 2008; Hytinen et al 2010; Čech and Tesařová 2015; Elaieb et al 2015; Xue et al 2016). Moreover, formaldehyde emission from wood is increased after heat treatment at higher temperatures (Schäfer and Roffael 2000).

In thermally modified softwoods, volatile terpenes and hexanal decrease after the heat treatment, whereas acetic acid and aldehyde furfural increase, as shown for Scots pine and Norway spruce (Hytinen et al 2010). After the heat treatment of Scots pine at 230°C for 24 h, volatile terpenes (α -pinene and 3-carene) decreased drastically from about 72 to 10% of total VOC emissions. Hexanal decreased from approximately 12

to 1%. By contrast, furfural increased from 0 to about 28%, carboxylic acids (acetic acid) and their esters from 0 to 30%, and acetone (2-propanone) from 0 to about 7% (together with four other ketones they increased from around 1 to 16%) of total VOC emission (Manninen et al 2002). This agrees with another study, where untreated pine predominantly emitted volatile terpenes (α -pinene, camphene, and limonene) and smaller amounts of hexanal and acetic acid. When treated at 180°C for 4 h, samples emitted volatile terpenes, acetic acid, and furfural. After 230°C for 4 h, mostly acetic acid, and small amounts of terpene α -pinene, and furfural were emitted (Mayes and Oksanen 2003). Similarly, emissions of volatile terpenes and hexanal from the untreated woods disappeared from Aleppo pine, maritime pine, and radiata pine after thermal treatment at 103°C, 170°C, and 230°C over 15 h. In the most severe treatments of these wood species, emissions of acetic acid were dominant, but vanillin and guaiacylacetone appeared along with furfural (Elaieb et al 2015). Spruce showed similar patterns after heat treatment, but they were not as drastic as in pine. There were significant decreases in volatile terpenes from approximately 95 to 65% (at 180°C and 200°C), and hexanal from 2 to 0% (at 180°C and 200°C) of total VOC emission. An increase was observed for carboxylic acids (acetic acid) from few to approximately 25% (at 180°C and 200°C) of total VOC emission. A substantial temperature-dependent increase in furfural from 0.3 to 1.5% at 180°C and to 9.3% at 200°C was observed by Peters et al (2008). Similarly, 5-methylfurfural increased from 0 to 0.8% at 180°C and to 0.5% at 200°C of total VOC emissions in heat-treated spruce wood. Both accounted for almost 100% of the aldehyde fraction (Peters et al 2008). This corresponds to a study on heat-treated Scots pine (at 212°C, 2 to 3 h) and Norway spruce (at 190°C, 2 to 3 h), where the emissions of acetic acid and furfural increased and those of hexanal and volatile terpenes significantly decreased when compared with their air-dried counterparts (Hyttinen et al 2010).

Aldehyde emissions (hexanal and pentanal) from thermally treated hardwoods decreased

drastically at higher temperatures, whereas emissions of acetic acid and furfural increased. This was observed in heat-treated European aspen (at 190°C, 2 to 3 h) (Hyttinen et al 2010), ash, beech, and sycamore maple (at 180°C and 200°C), where 5-methylfurfural was also observed (Peters et al 2008). In thermally treated Chinese white poplar sapwood, the most significant VOCs were aldehydes 2-nonenal (at lower temperatures of 160°C and 180°C for 2 h) and furfural (at higher temperatures of 200°C and 220°C for 2 h), whereas oxalic acid (dicarboxylic acid), the main compound emitted from the untreated wood, decreased completely after the treatment. Moreover, at higher temperatures (above 200°C for 2 h), aromatic compounds, such as phenol, and esters were detected (Xue et al 2016). Similar results were obtained with thermally treated white poplar (at 180°C and 200°C), where furfural and phenol emissions increased with heat treatment temperature (Čech and Tesařová 2015).

Formation of New VOCs

Thermal degradation of wood components (ie hemicelluloses, cellulose, lignin, and extractives) during heat treatment leads to the formation of new products and by-products, including VOCs that can be emitted from wood after the treatment (Esteves and Pereira 2009; Poncsak et al 2009; Culleré et al 2013; Wang et al 2018). Thus, the amount of VOCs, including acids, aldehydes, aromatics, alkanes, and some trace compounds (eg furans, ketones, phenols, and esters) increase with an increase in heat treatment temperature, whereas those of alcohols and alkenes decrease. This has been clearly demonstrated in a study on thermally treated southern yellow pine (*Pinus* spp.) wood, where the number of VOCs increased with heat treatment temperature, although the total VOC quantity emitted is decreased in thermally treated softwoods. There were 86, 93, and 131 VOCs identified in untreated specimens, specimens heat treated at 140°C, and specimens heat treated at 220°C, respectively (Wang et al 2018).

Hemicelluloses thermally degrade more readily than cellulose or lignin and at 200°C, start producing large quantities of volatiles, including carboxylic acids (mainly acetic and formic acids), aldehydes (mainly furfural), and ketones (acetone and others) (Manninen et al 2002; Peters et al 2008; Hyttinen et al 2010; Xue et al 2016). Degradation of hemicelluloses starts by deacetylation as acetyl groups are hydrolyzed and acetic acid is formed. High temperatures increase the content of acetic acid, which is one of the most abundant compounds in VOC emissions from heat-treated wood, although it is formed even at low temperatures (Esteves and Pereira 2009). Further hemicellulose decomposition leads to the formation of aldehydes, such as furfural and hydroxymethylfurfural, which are degradation products of pentoses and hexoses, respectively; as well as 5-methylfurfural (Peters et al 2008; Esteves and Pereira 2009). As the temperature increases to 220°C, hydroxyl and carboxyl groups react and form esters, in which content is increased, whereas alcohol and acid contents decrease. With increasing temperature, the alkane content also increases, presumably because of pyrolysis of hemicelluloses (Wang et al 2018).

Thermal degradation of *cellulose* results in levoglucosan, an important primary degradation product, and finally furan and its derivatives are formed as end products of heat-treated cellulose (Manninen et al 2002). Alkylfurans, such as ethyl-, propyl-, and pentylfurans, are thermal decomposition products of cellulose and other polysaccharides. They are also generally found in untreated hardwood and, therefore, are most likely formed during VOC analysis at an elevated temperature (Risholm-Sundman et al 1998; Stachowiak-Wencek and Prądzynski 2014).

Volatile aromatic compounds can be formed as degradation products of *lignin* or derived from the breakdown of the bonds connecting lignin to hemicellulose at high temperatures (Gao et al 2013) and increase considerably with heat treatment temperature (Wang et al 2018). Phenol and phenolic organic compounds were newly formed from thermal decomposition of lignin at

high temperatures (Gao et al 2013) in heat-treated Chinese white poplar (Xue et al 2016) and in white poplar (Čech and Tesařová 2015). Moreover, the aromatics vanillin and guaiacylacetone appeared during the most extreme treatments (15 h duration, setpoints at 103°C, 170°C, and 230°C) of Aleppo pine, radiata pine, and maritime pine wood (Elaieb et al 2015). In thermally treated southern yellow pine, 1-methoxy-4-(2-propenyl)-benzene (estragole) was the main aromatic compound, and in addition, many new aldehydes were identified, some of them can also be generated by the degradation of lignin during the heat-treatment process (Wang et al 2018).

Wood *extractives* including fatty acids, glycerides, resin acids, steroids, steryl esters, waxes, and terpenes can readily evaporate or degrade during the heat treatment giving new product emissions of VOCs or semi-VOCs (Mayes and Oksanen 2003; Hyttinen et al 2010). For example, terpenes from softwoods such as camphene, 3-carene, and limonene may degrade to aromatics such as 1-methyl-4-(1-methylethenyl)-benzene (*p*-cymene) and 1-methyl-2-(1-methylethyl)-benzene (*o*-cymene) (Mcgraw et al 1999). Aromatic degradation products have been found in thermally treated pine and spruce; however, they were also detected in greater quantities in air-dried softwood samples, and are, therefore, probably at least partly formed during VOC analysis at 250°C (Hyttinen et al 2010; Wang et al 2018). On the other hand, as mentioned before, fatty acids are degraded (oxidized) to aliphatic aldehydes such as hexanal, which is accelerated at high temperatures (Gabriel et al 2015) and can be further oxidized to hexanoic acid (Englund 1999).

FACTORS THAT INFLUENCE VOC EMISSIONS FROM WOOD

Variability in wood VOC emissions observed between different studies or wood samples has been attributed to the fact that wood is a variable and complex multicomponent biopolymer and its emissions are influenced by a number of factors (Englund 1999). These factors should be taken into account when studying wood VOC

emissions to prevent certain factors to impact VOC emission measurements, and are recommended to be described thoroughly to allow reliable interpretation of the results and to ensure comparability. Emissions of individual wood VOCs depend on endogenous factors, including genetic and biochemical factors (eg wood species and type); and on exogenous (biotic and abiotic) factors, such as growth conditions, wood treatment, etc. (Englund 1999; Roffael 2006; Wolpert 2012). Factors influencing VOC emissions are described in Table 2.

CONCLUSIONS

Wood, either untreated or thermally modified softwood or hardwood, contains and emits VOCs, which are collectively referred to as “wood VOCs”. They are present in wood because of their biological function in a tree (primary VOCs, such as volatile terpenes) or are formed during degradation processes of wood (secondary VOCs, such as hexanal and acetic acid). Wood VOCs are emitted into the indoor built environment, where they can have various negative or positive effects on occupants and can significantly impact indoor air quality, and accordingly, human well-being and health.

However, wood is a complex multicomponent biopolymer showing great variability, which is also reflected in the emissions of VOCs. Variability has been observed for VOC emissions or emission rates and is attributed to numerous endogenous and exogenous factors, including wood species, type of wood sample (heartwood and sapwood), growth conditions, wood treatment, etc. (described in Table 2). Therefore, when analyzing VOCs emitted from wood, these factors must be considered to reduce their impact on the measurements. It is recommended they be described in detail to allow reliable interpretation of the results and to ensure comparability.

Studies reviewed in this article provided reasonably consistent results regarding the wood VOCs identified in individual wood species. The general emission patterns of softwoods and hardwoods are clear-cut, indicating that the

findings can be generally applicable. Changes that occur in VOC emissions from thermally modified wood after heat treatment are also generally consistent throughout the reviewed studies (Table 1).

This review article revealed the following general conclusions:

1. Softwoods (particularly pine, followed by spruce) emit the highest concentrations of wood VOCs because of large emissions (70-90%) of volatile terpenes (monoterpenes and sesquiterpenes) that gradually decrease over time. In addition, softwoods also emit low concentrations (up to 25%) of hexanal and acetic acid.
2. VOC emissions from hardwoods are considerably lower (roughly 50 times) than that of softwoods because they do not contain volatile terpenes, but instead emit low concentrations of hexanal and pentanal, as well as acetic acid and other VOCs, which are formed during wood degradation processes.
3. The vast majority of the studies reviewed in this article used sampling methods that are unsuitable for the analysis of formaldehyde, acetaldehyde, formic acid, and methanol. Therefore, they are typically not detected, although their emissions can also occur; eg formaldehyde emissions are ubiquitous, albeit at low concentrations, and increase after heat treatment at higher temperatures.
4. After heat treatment, the total quantity of VOCs emitted from thermally modified softwoods are lower compared with those from their untreated counterparts because of the removal of large amounts of volatile terpenes during the heat treatment. By contrast, in thermally modified hardwoods, total VOC emissions are increased compared with those from their untreated counterparts because they only emit VOCs formed during wood degradation processes, which is facilitated at high temperatures.
5. In thermally treated softwoods, emissions of volatile terpenes and hexanal are drastically decreased, whereas emissions of acetic acid, as well as newly formed furfural and other

compounds are increased. Similarly, in thermally treated hardwoods, the emissions of hexanal and pentanal are reduced, whereas acetic acid and furfural increased. The latter two are both degradation products of hemicelluloses at high temperatures.

6. The number of VOCs emitted from thermally modified wood increases with heat treatment temperature.

Further research should seek to provide a better understanding of the emissions of VOCs from wood and especially from thermally modified wood, as well as their variability, by considering a variety of factors influencing VOC emissions, including thermal treatment processes. Furthermore, mathematical models should be developed to predict the emission properties of (thermally modified) wood under various conditions and treatment processes. Thus, the expected concentrations of individual wood VOCs emitted from wood and thermally treated wood products can be assessed in indoor air, and their impact on indoor air quality can be evaluated.

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