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DISSERTATION

Methods for measurement, reduction and evaluation of VOC emissions from engineered softwood panels

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der technischen Wissenschaften unter der Leitung von

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Abstract

In the past twenty years, the scientific interest towards characterization of volatile organic compounds (VOC) emitted indoors arose rapidly. The main reason for this is the construction of energy-efficient buildings with reduced indoor air exchange rates resulting in an increased exposure of the occupants to VOC.

Engineered softwood panels are often a pronounced VOC source and as such an assessment of their VOC emissions potential (and in respect with the demands of the current indoor air quality labeling schemes) should be done and if necessary a reduction of certain emissions should be aimed at.

In the present doctoral thesis a biotechnological approach was taken to address the problem of aldehyde emissions by using microorganisms - fungi and bacteria - capable of metabolizing aldehyde precursors (unsaturated fatty acids). Reduction of more than 60% of aldehydes emissions from laboratory panels was achieved. The concentrations of unsaturated fatty acids in the treated panels were also reduced in this range. In terms of analytical methodology, headspace-SPME-GC/MS analytics established itself as a convenient tool for screening for microorganisms capable of reducing aldehyde emissions.

The utilization of so-called Micro-Chambers for the purpose of characterizing VOC emissions from engineered wood panels showed high potential especially after the implementation of a humidity control unit. The analytical methods employed in the experiments were refined and further developed resulting in the adaptation and the usage of the micro-chamber humidifier as novel method for characterization of VOC present in dry-kiln condensates.

In the field of indoor air quality (IAQ) evaluation schemes assessment it was shown that these schemes should also be evaluated in order for the industry to rapidly trace problematic substances and to adapt its production processes to changes in IAQ assessment schemes. In this work, the author proposes a mechanism for applying such evaluation in order to estimate the restrictiveness of evaluation schemes towards industrial production. Furthermore, the safety margins of IAQ evaluation schemes towards softwood-based products were estimated. It was established that the evaluation of softwood VOC emissions according ISO 16000-9 under certain conditions can lead to overestimation of the emissions with factors from 2 to 20 when compared with close-to-reality measurements.

Unpublished data from experiments of the author aiming at VOC reduction as well as considerations regarding the critical points of VOC measurement techniques by means of small-scale analytics can be found in the appendix of this work.

Eigenständigkeitserklärung

Ich bestätige mit meiner Unterschrift, dass ich die Dissertation selbstständig verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und mich auch sonst keiner unerlaubten Hilfe bedient habe. Weiters bestätige ich, dass ich diese Dissertation bisher weder im Inland noch im Ausland in irgendeiner Form als Prüfungsarbeit vorgelegt habe.

Wien,
10.01.2018 Dipl.-Ing. Daniel Stratev

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Index

Abbreviations

AgBB - Committee for Health-related Evaluation of Building Products (from German)
CFD - Computational fluid dynamics
CLT - Cross laminated timber
DACH - Area in Europe which includes countries with German as (one of) their nationwide official language(s), as well as dependent territories with German as a co-official language. The three major German-speaking countries (Germany [D], Austria [A], Switzerland [CH]) are commonly denoted as the DACH area.
DNPH - (2,4-)Dinitrophenylhydrazin
ECA-IAQ - European Collaborative Action Indoor Air Quality and its Impact on Man
FID - Flame ionization detector
GC/MS - Gas chromatography/mass spectrometry
GUT - Association of Environmentally Friendly Carpets (from German)
IAQ - Indoor air quality
IST - Internal standard
LCI - Lowest concentration of interest
µCTE - Micro-chamber (Markes)
NOAEL - No observed adverse effect level
OSB - Oriented strand board
RI - Retention index
SPME - Solid phase micro extraction
SVOC - Semi-volatile organic compounds
TD - Thermal desorption
UF - Urea formaldehyde
UFA - Unsaturated fatty acids
VOC - Volatile organic compounds
VOC* - General term for volatiles introduced by the author (including VVOC, VOC, SVOC, NH_3 etc.) without considering the differences in volatility or the presence of organic carbon
VVOC - Very volatile organic compounds
WHO - World health organization

1. Introduction

1.1. Definitions

In order to facilitate the understanding of the following contents, the intended meaning of some frequently used terms and abbreviations are specified in the following:

Volatile organic compounds (or VOC) are organic substances (usually liquids at ambient conditions) with low enthalpy of evaporation or, in other words, such compounds which need less energy to evaporate. VOC are characterized by relatively high vapor pressure (occurrence in the gas phase) at room temperature as well as by relatively low boiling points. VOC are very prone to be analyzed (separated) by means of gas chromatography (GC) because they tend to be present in both stationary and mobile phase of a GC column.

Since the term "low" related to enthalpy or temperature is conventional, a delimiter is needed in order to categorize the organic compounds in accordance with their volatility. Different institutional bodies around the world give different practical definitions regarding the term VOC:

A physical definition (European Parliament 3/11/1999) defines VOC as any organic compound having a vapor pressure at 20°C of 0,01 kPa or more.

Figure 1 shows the dependency of the equilibrium concentrations in the gas phase (over pure liquid) on temperature for several volatiles calculated by using Equation 1 and data for the vapor pressure at two different temperatures.

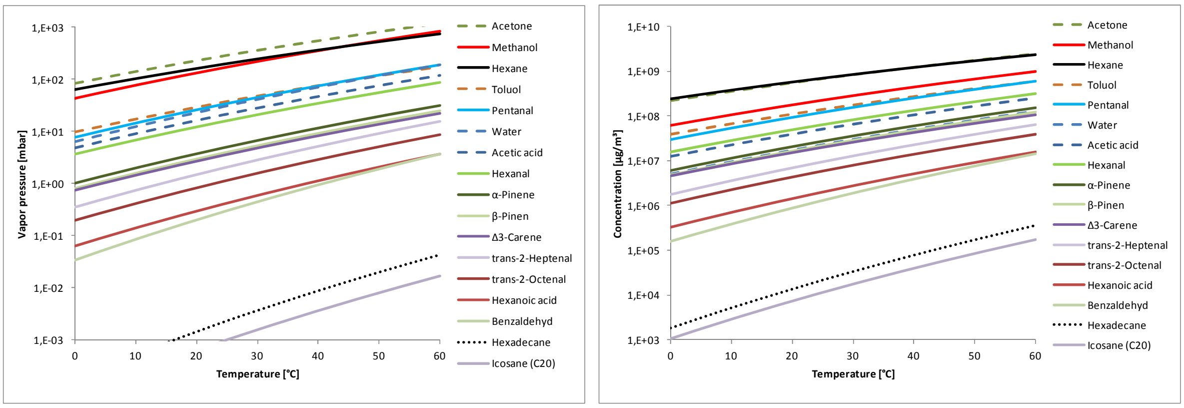

Figure 1. Calculated dependency of equilibrium gaseous vapor pressure (left) and concentration (right) of different volatile substances on temperature

$$\ln p1 - \ln p2 = \frac{\Delta H_v}{R}\,\frac{T_2 - T_1}{T_1 T_2} \qquad \text{(Equation 1)}$$

Since vapor pressure at 20°C correlates with the boiling point of the substances (assuming isobaric conditions and stability of the chemical structure), a logical restatement of this definition is to use boiling point as a delimiter.

Such classification of the volatile organic substances into several groups according to their boiling points was done by the World Health Organization (WHO 1987) (Table 1).

Table 1. Classification of volatile organic compounds according WHO and AgBB

Abbreviation	Word or phrase	Boiling point (WHO)	Elution range (AgBB)
VVOC	Very Volatile Organic Compounds	< 0 up to 50…100 °C	< C6*
VOC	Volatile Organic Compounds	50…100 up to 240…260 °C	C6-C16
SVOC	Semi-Volatile Organic Compounds	240…260 up to 380…400 °C	C16-C22
POM	Organic compound associated with particulate matter or particulate organic matter	> 380 °C	-

* Not explicitly specified (2015)

It should be pointed out that WHO definition did not put stringent bounds between neighboring groups. Examples for VVOC according to WHO definition are formaldehyde, butane, isoprene, dichloromethane and acetone. VOC are benzene, toluene, acetic acid, pentanal, monoterpenes, cyclodecane, naphthalene and decanal. Diethyl phthalate, higher alkanes (C15-C24), anthracene and carbazole are belonging to the SVOC.

The third definition of interest with biggest impact on this work is that of the instrumental analytical chemists (ISO 16000-6:2004; UBA Deutschland) who separate volatile substances into the same subgroups as WHO but accordingly to their elution-times (also known as retention times – RT) from an apolar gas chromatography capillary column[1].

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[1] Initial steps of developing this definition were done in 1997 in two reports of a working group of the European comission ECA-IAQ 1997a, 1997b where the “TVOC quantity” was specified. According to these reports TVOC (or total volatile organic compounds) is the sum of the masses of all compounds eluting from an apolar GC-column in the elution range from n-hexane to n-hexadecane, divided by the sampled air volume. Seven years later the TVOC definiton was adopted from the International Organization for Standardization ISO 16000-6:2004 in parallel to the existing WHO definition and implemented in the German regulatory framework UBA Deutschland where only the substances inside the TVOC’s elution range (C6-C16) are declared as VOCs and the SVOCs are compounds which elute in the range C16-C22.

In addition it should be taken into account that the term “VOC” is sometimes wrongly used for general denotation of volatile substances in the gas phase without considering enthalpy of evaporation or origin (organic or inorganic). In this thesis the author has chosen to use VOC* as the abbreviation for generally referring to volatiles.

The overview above clearly shows that there is no consensus how to define the term VOC and each scientific group uses its own delimiter which appears to be most suitable for the corresponding application field. Although this approach could not be considered for being wrong, it undoubtedly leads to misconceptions.

1.2. Why are volatile substances of growing importance

There are two major factors which increase the importance of volatiles for the occupants: In order to reduce energy costs modern buildings are constructed gas-tight and in cases where no dedicated ventilation system is available it is therefore possible that the manually regulated air exchange rate is not sufficient for the emitted volatiles to be removed from the premises. Thus, the occupants’ exposure to volatile compounds might be higher than expected. The second important consideration is that the average person spends most of his/her time indoors (90% for USA) (OECD 2005).

The combination of high concentrations of volatiles and long-term exposure of occupants motivated the corresponding authorities in some countries to take measures for evaluation and regulation of the health related risks. It should be pointed out that the health related risk depends mainly on the type (chemical structure), the combination and the concentration of the chemical substances which form the VOC immissions as well as on the duration of exposure and that there is no general nonspecific, cumulative safety threshold (ECA-IAQ 1997b; Seifert 1999).

1.3. Research issues

At the beginning of this work the author faced several research issues. First of all it was the uncertainty within the community caused by the negative acceptance of softwood (more precisely pinewood) in the DACH region as a raw material for the production of engineered wood panels due to its comparatively VOC emissions[2]. It was therefore of interest to identify the substances which contribute to this negative evaluation and to quantify their particular contribution to the problem. Another important issue was to explore whether there were ways for effectively reducing emissions of typical pine-wood VOC from the end products.

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[2] According to ECA-IAQ Report 18 and its derivative evaluation schemes

In order to address these research issues, a methodical challenge was to adapt a preselected analytical system (Micro-Chambers from Markes) for conducting VOC emission measurements in an appropriate way and to explore the comparability of the results with other, larger scale systems. The topics were (1) to construct and implement an appropriate humidity control for the system, (2) the characterization of the fluid dynamics (air velocity) above the surface of the tested objects, and (3) the comparison with measurements conducted in larger chambers (225 L or 1 m³). Another methodical challenge was to validate an analytical method at TU Wien for GC/MS-TD identification of VOC/SVOC (Agilent 7890A/5975C with PTV and CTC-PAL autosampler).

As a cross-cutting theme, the efficiency of IAQ evaluation schemes towards softwood and their influence on industrial production was also evaluated. The reference (also known as model-) room concept was examined by putting focus on engineered softwood products. Very important for the evaluation of the IAQ are the (measured or derived) VOC concentrations for day 28 (after the start of a chamber test). The VOC concentrations at day 28 are used by IAQ evaluation schemes for assessment of the chronic intoxication risk for the inhabitants. Since it appeared likely that the VOC emissions from softwood products and indoor VOC concentrations at day 28 are not in steady state and are further declining with time, it was of interest to estimate the safety margin when choosing day 28 as an assessment time point. Another topic was to develop a concept for prediction of the impact of evaluation schemes changes on industrial production.

A VOC issue which certainly accompanies the engineered wood panel production was the characterization of the VOC which are generated during the production process and are present in the dry-kiln condensate formed during wood drying. Since headspace-SPME or two phase extraction as the conventional VOC isolation and analysis methods were found not to be sensitive enough, an alternative novel extraction technique was developed and employed.

2. Methodology

The following scientific methodology and equipment were used for investigating the research issues summarized above and described in the scientific publications. Full details of the methods are given in Appendix II:

- Tenax-TD-GC/MS analytics of the VOC* emissions consisting of Agilent 7890A/5975C GC/MS system, equipped with a Chromtech TDAS 2000 thermal desorption unit, programmable temperature vaporization (PTV) injector and HP-PONA column (methyl siloxane, 50 m=0.2 mm i.d.=0.5 mm) (Stratev et al. 2011);

- Validated HPLC-based analytics for formaldehyde consisting of Thermo Scientific LPG-3400SD pump with WP-3000SL autosampler, Thermo Scientific Acclaim Carbonyl C18, 3 µm 120A 3.0 x 150 mm column, and UV-VIS DAD-3000 detector (as described in 9.2.2);
- Micro-Chamber measurements of the VOC emissions in the style of ISO 16000-9 by using Markes® µCTE120 Micro-Chambers and self-developed cell independent humidity control (Stratev, Srebotnik 2011);
- Headspace-SPME-GC/MS (or FID) analytics for the screening of VOC-reducing strains by using a 75 µm CAR/PDMS SPME fiber (Supelco) and 20 ml headspace vials (Stratev et al. 2009);
- Use of standard microbiological methods for cultivation (on agar plates) and identification of cultures (API 20);
- High pressure extraction, derivatisation (silylation) and GC/MS for the analytics of extractives by employing a Retsch ZM200 centrifugal mill equipped with a 2 mm sieve for samples comminution, Christ Alpha 1-4LD for wood drying, a Büchi SpeedExtraktor E-916 for extraction of analytes, a HP5 MS column (30 m, 0.25 mm) for chromatographic separation and MS/FID for detection;
- Self-developed purge and trap (on Tenax™) analytics for the dry-kiln condensate analysis (Figure 45, Appendix II) (Rathke, Stratev 2013);
- ANOVA for the statistical evaluation of the results by using Design Expert 7 software;
- Application of established nonlinear iterative algorithms (Excel-Solver) for modeling development of VOC emissions as described in the EN 717-1 standard;
- CFD simulation programs for calculating and visualizing the air velocity in the Micro-Chambers by using Gambit v2.3 for constructing the virtual geometry (mesh) and Fluent v 6.3 for fluid modeling as described in 9.4.1 (Appendix II)

3. Summary of the scientific publications

The emissions of the following substances which belong to the groups of monoterpenes and aldehydes were found to be problematic for the health-risk evaluation of softwood-based construction products according to the majority of DACH-IAQ-evaluation schemes: α-pinene, 3-carene, β-pinene, hexanal, pentanal and octanal (Stratev et al. 2011; Stratev et al. 2016b; Stratev et al. 2016a). Preliminary data of the author showed that also limonene, heptenal and octenal emissions could be equally problematic for softwood-based products. Although the emissions at day 28 of the single compounds listed above rarely exceed the corresponding LCI-values, the additional cumulative rules in the IAQ-evaluation schemes (such as TVOC- or the R-rules) contribute to an increased risk of a negative evaluation and rejection of the respective construction product. Unpublished results of the author suggested that α-pinene, 3-carene, hexanal and limonene are more likely to be affected by the TVOC rule, while heptenal, octenal and hexanal increase the risk for the product of not complying with the R-rule. From this point of view the reduction of aldehyde emissions appeared more purposeful since it would decrease the risk of violating both the TVOC- and the R-rules.

In the present doctoral thesis a biotechnological approach was taken to address the problem of aldehyde emissions by using microorganisms (fungi and bacteria) capable of metabolizing unsaturated fatty acids (UFA). UFA are the predominant precursors of aldehydes in wood material and their removal by microorganism therefore significantly reduced further aldehyde emissions from treated softwood (Stratev et al. 2011; Stratev et al. 2016b). As an example, the treatment of wood strands with an albino mutant of a non-destructive blue stain fungus (Cartapip 97®) resulted in a 60–78% reduction of the pentanal and the hexanal emissions from the produced laboratory OSB boards during the observation period of 28 days (Stratev et al. 2011). Pellets produced from pine chips treated with another blue stain fungus, *Ceratocystis coerulescens*, for 4 weeks at room temperature also showed reduction in their aldehyde emissions by more than 75% for at least 6 weeks after their production (Weigl et al. 2015b). In this case the selected fungal strain was not an albino mutant and a coloration of the treated pellets was thus observed. However, the staining was not considered as a disadvantage for this type of application.

The use of so-called biofilms also showed great potential for metabolizing wood extractives responsible for VOC emissions (Stratev et al. 2016b). Biofilms are ubiquitous in many aqueous and solid substrates and are supposed to also grow on effluents collected or stored in ponds or basins of industrial plants. In this work, process waters from two reservoirs (called site I and site II) of a wood panels producing plant were used as inoculum containing specialized and preconditioned microorganisms. Laboratory boards made from strands treated with effluents from site II exhibited a higher aldehyde emission at the beginning of the analysis period (days 3–7) than did untreated control and site I samples. From day 17 on, an expected increase in the aldehyde concentration of the untreated samples was observed, most probably as a result of intensified UFA oxidation. By contrast, the emissions of aldehydes from treated samples remained almost constant and were significantly lower than those of the untreated control samples. Thus, it was proven that undefined microbial consortia (biofilms) isolated from suitable sources in the production plants are capable of reducing aldehyde emissions through metabolism of aldehyde precursors.

GC/MS extractives analysis of treated material revealed that both fungi and microbial consortia (biofilms) are capable of degrading unsaturated fatty acids by up to 60-75% for the period of treatment (4 to 6 weeks at approx. 23°C). This decrease was in good agreement with the measured decrease of aldehyde emissions from treated samples. The application of microorganisms also reduced the concentrations of other common nutrients, particularly sugars or sugar alcohols present in softwood and thus pretreatment with blue stain fungi or biofilms could also be considered as a wood preservation tool.

An interesting consequence of Cartapip 97® treatment was the cleavage of the stilbene-type molecules pinosylvin or pinosylvin monomethyl ether present in softwood to 3,5-dihydroxybenzyl alcohol, 3,5-dihydroxybenzoic acid or 3-hydroxy-5-methoxybenzoic acid (Stratev et al. 2011). A similar behavior was observed when using another wild-type blue stain fungus identified as *Sphaeropsis sapinea* (NCBI PopSet 254847657, unpublished results).

In terms of analytical methodology headspace-SPME-GC/MS-analytics established itself as a convenient tool for screening for microorganisms capable of reducing aldehyde emissions. Measurements strongly indicated that reduced (or more exactly suppressed) aldehyde emissions during the incubation of microorganisms on sterilized sapwood particles correlated with the metabolism of UFA (Stratev et al. 2009). Consequently headspace-SPME-GC/MS could be used as standalone research method without supporting extractives analytics. This technique has proven beneficial for monitoring microbial activity also because it is sensitive enough to identify aldehyde suppressing strains at the very early stages of their incubation (≤ 48 hours on sterilized softwood particles).

The utilization of so-called Micro-Chambers for the purpose of characterizing VOC emissions from engineered wood panels showed big potential especially after the implementation of a humidity control unit (Stratev, Srebotnik 2011). Since humidity is known as a critical parameter for the formation of formaldehyde emissions, it may be expected that other VOC*-emissions (acetic acid, furfural, etc.) are also influenced by air humidity. Micro-Chambers with independent control of the humidity in each cell (as shown in Figure 38, see 9.4.3) could be easily used for 2D experimental designs in order to examine the dependency: *Emissions=f(RH%, T)*. Micro-Chambers proved to be a suitable tool for research and product development (see 9.4). On the other side, the evaluation of VOC emissions using Micro-Chambers showed considerable overestimation of the TVOC concentrations when comparisons with standard test methods were done (unpublished data). The observed differences in the results when compared with larger scale test chambers or model rooms could be traced to improper strategy for sampling assembly in the test chamber, scaling (edge) effects and VOC permeability of the sealing tape (see 9.3). However Micro-Chambers should be preferred for relative comparisons in cases where no correlation with norm methods is needed or when the mechanism of the VOC transport is to be characterized (see 9.3.3).

In the field of IAQ evaluation schemes assessment it was shown that such schemes should also be evaluated in order for the industry to rapidly trace problematic substances and to adapt its production processes to changes in the IAQ assessment schemes (Stratev et al. 2016a). In this work, the authors propose a mechanism for applying such evaluation and to estimate the restrictiveness of a certain evaluation scheme. It was also confirmed that VOC concentrations on day 28 in constructions made of engineered softwood are not steady state long-term concentrations but further decrease after day 28. The resulting concentration safety margins when comparing the (whole data model) values at day 28 with the values at day 180 (6 M) were between 2 and 7 and those for the one year period were between 2 and 21.

The self-developed humidity control unit was slightly modified and used as purge and trap (on Tenax™) device for determination of diluted wood-typical VOC in aqueous solutions like dry-kiln condensates (Rathke, Stratev 2013) to address the problem that standard two-phase extraction analytical techniques in apolar solvents like MTBE were not sensitive enough due to considerable VOC losses in the concentration (solvent evaporation) step. In contrast, purge and trap established itself as a novel and simple method for analysis with even better sensitivity than headspace-SPME techniques, enabling the identification and quantification of the following VOC present in the kiln drying condensates: (i) terpenoids, (ii) ketones, (iii) alcohols, and (iv) traces of aldehydes and aromatic compounds. Small traces of benzene were found in the spruce condensate, but the concentrations were below the regulated limits. An interesting observation was that the fractions of alcohols and ketones were much higher than their usual fractions as detected by direct emission determination of the corresponding dry wood materials. This fact could be explained with the higher solubility of polar ketones and alcohols in water compared to terpenes resulting in their selective concentration in the condensate. Furthermore, high temperatures and moisture content during the drying process may also contribute due to the oxidation of the monoterpenes.

The scientific publications summarized above collectively contribute to a better understanding of IAQ issues and provide new methods for VOC analysis and control. More specifically, the problematic VOC for softwood-based construction products were defined and resulted in the proposal of methods for reduction of aldehydes through pretreatment of the raw material with fungi or unspecified microbial consortia (biofilms). Furthermore, the safety margins of IAQ evaluation schemes towards softwood-based production were estimated and a proposal for estimation of the restrictiveness of IAQ evaluation schemes was made. Standard analytical methods initially employed in the experiments were refined and further developed resulting in the adaptation and the usage of small-scaled chambers for the characterization of VOC emissions as well as novel methods for characterization of VOC present in dry-kiln condensates.

4. List of publications constituting the present doctoral thesis

4.1. Peer-reviewed scientific publications

- Stratev, D.; Gradinger, C.; Ters, T.; Fackler, K.; Kuncinger, T.; Srebotnik, E. (2011): Fungal pretreatment of pine wood to reduce the emission of volatile organic compounds: Holzforschung: 65.

  Contribution of Daniel Stratev*: Conception of the study, experimental design, selection of test methods, sampling and analysis, data interpretation, literature research, writing and editing of the manuscript*

- Stratev, D.; Günther, E.; Steindl J.; Kuncinger, T.; Srebotnik, E.; Rieder-Gradinger, C. (2015): Industrial waste water for biotechnological reduction of aldehyde emissions from wood products: Holzforschung: 69.

  Contribution of Daniel Stratev*: Conception of the study, experimental design, selection of test methods, sampling and analysis, data interpretation, literature research, writing and editing of the manuscript*

- Weigl, M, et al. (2015): Processing pellets towards low emissions. Select Presentations from the 3rd International Conference on Processing Technologies for the Forest and Biobased Products Industries (PTF BPI 2014), September 24-26, 2014, Kuchl, Austria: 65, 3-4: S74-S81.

  Contribution of Daniel Stratev*: Data analysis, data interpretation, literature research, writing and editing of the manuscript*

- Rathke, J and Stratev, D (2013): Analysis of the Chemical Constituents of Dry-Kiln Condensate and its Technological Recovery – Part 1: Volatile Extractives: Bioresources: 8(4): 5783–5793.

  Contribution of Daniel Stratev*: Experimental design, selection of test methods, sampling and analysis, data interpretation, literature research, writing and editing of the manuscript*

- Stratev, D., Hansmann, C., and Rathke, J. (2015): Analysis of the Chemical Constituents of Kiln-dry Condensate and its Technological Recovery – Part 2: Semi-volatile and Volatile Extractives: Bioresources: 10(2).

  Contribution of Daniel Stratev*: Experimental design, selection of test methods, sampling and analysis, data interpretation, literature research, writing and editing of the manuscript*

- Stratev, D.; Fürhapper, C.; Niedermayer, S.; Habla, E.; Nohava, M.; Weigl, M. (2016): From model rooms towards a modelled indoor environment. In: International Wood Products Journal 7 (4), S. 195–201.
- Contribution of Daniel Stratev*: Conception of the study, selection of modeling approaches, data analysis, data interpretation, literature research, writing and editing of the manuscript*

4.2. Further thesis-related publications and patents

- Stratev, D.; Ters, T.; Gradinger, C.; Messner, K.; Fackler, K. (2009): Impact of fungal activity on VOC emissions from pine wood particles. In: Lenzinger Berichte 87, S. 11–15.

  Contribution of Daniel Stratev*: Conception of the study, experimental design, selection of test methods, sampling and analysis, data interpretation, literature research, writing and editing of the manuscript*
- Gradinger,C., Stratev,D., Boisselet,T., Schieferbein,J., Messner,K. and Fackler,K. (2009): Molecular characterization of Diplodia pinea isolates from Central Europe: NCBI PopSet 254847657 : https://www.ncbi.nlm.nih.gov/popset/254847657

  Contribution of Daniel Stratev*: Primers design, sampling and analysis, data interpretation*
- Stratev, D., Srebotnik, E. (2011) Verfahren zum Überführen von in einem Material enthaltenen Substanzen in die Gasphase. Austrian Patent Application No. AT 512 096 – 2013-05-15.

  Contribution of Daniel Stratev*: Conception, technical design, selection of test methods, sampling and analysis, data interpretation, writing and editing of the manuscript*
- FRITZ EGGER GMBH & CO. OG (2014): Verfahren zur Herstellung eines Holzwerkstoffs. Kuncinger, T., Gradinger, C., Stratev, D. Int. Patent Appl. WO2014064209A1.

  Contribution of Daniel Stratev*: Conception, experimental design, selection of test methods, sampling and analysis, data interpretation, writing and editing of the manuscript*

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Rathke, Jörn; Stratev, Daniel (2013): Analysis of the Chemical Constituents of Dry-Kiln Condensate and its Technological Recovery – Part 1: Volatile Extractives. In *Bioresources* 8 (4), pp. 5783–5793.

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Stratev, Daniel; Fürhapper, Christina; Niedermayer, Sabrina; Habla, Elisabeth; Nohava, Michael; Weigl, Martin (2016a): From model rooms towards a modelled indoor environment. In *International Wood Products Journal* 7 (4), pp. 195–201. DOI: 10.1080/20426445.2016.1222254.

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6. Curriculum vitae

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Aus- und Weiterbildung

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2002 bis 2008	**TU-Wien –** Biochemie, Biotechnologie und Lebensmittelchemie Dipl.-Ing.
2008	Akademischer Grad: Dipl.-Ing.
2008	Diplomarbeit mit Thema: Einfluss von Pilzen auf die Qualität von Kiefernholz: Biokontrolle, Harzabbau und Emissionskontrolle
1996 bis 2002	**UCTM-Sofia** - Technische Ökologie und Umweltschutz
2002	Akademischer Grad: Magister
2002	Diplomarbeit mit Thema: Anwendung der Lattice-Boltzmann-Methode für die Modellierung von sorptiven Prozessen in gepackten Säulen

Wien 01.1.2018

Wissenschaftliche und anwendungsorientierte Projekte

2009 - 2010	**Etablierung einer small-scale Methode zur Bestimmung der VOC** Emissionen (Patent TU-Wien);
2009 - 2013	**Reduktion der VOC Emissionen aus Holz-Produkten** mittels mikrobieller Behandlung der Rohstoffe (Patent Fa. EGGER);
2012 - 2018	**Projekte zur Charakterisierung der sorptiven Eigenschaften** von Baumaterialien und Innenraum-Produkten;
2014	Etablierung einer akkreditierten analytischen Methode **zur Formaldehyd-Bestimmung nach ISO 16000-3** (HPLC/DNPH-Methode);
2014 - 2015	Entwicklung und Etablierung von Methoden zur **Bestimmung und Reduktion der VOC** Emissionen aus Pellets;
2015 - 2017	Optimierung der **Zugabe von Komplexbildnern bei der Herstellung von Papier und Zellstoff.** Entwicklung und Etablierung von **Methoden zur Bestimmung von Komplexbildnern;**
2016	Etablierung einer akkreditierten analytischen Methode (nach DIN EN ISO 16994) **zur Bestimmung des Gesamtgehaltes an Schwefel Chlor und Fluor in biogenen Festbrennstoffen** mittels Ionenchromatographie**;**
2016 - 2017	**Charakterisierung des Einflusses von holztypischen VOC auf die hygroskopischen Eigenschaften von Zeolithen;**
2017 - 2018	Etablierung einer **Methode zur Bestimmung von VVOC, CO$_2$, CO und NH$_3$** mittels FTIR.

Wissenschaftliche Beiträge in Konferenzen

- **Stratev D** et al. (2010) **Fungal influence on VOC emission from pine wood** particles. Poster: 1st Symposium on Biotechnology Applied to Lignocelluloses, in: "Lignobiotech One", 28.03.2010 - 01.04.2010, Reims, Frankreich
- Gradinger C, **Stratev D** et al. (2010) "**Biological control of the blue-stain fungus** Sphaeropsis sapinea **in the field**"; Poster: 11th European Workshop on Lignocellulosics and Pulp, in: "Proceedings", 16-19.08.2010, Hamburg, Deutschland
- Weigl M et al. (2014) Reducing VOC emissions from pellets by means of pre-treatment and processing, Second international workshop on pellet safety, 05.2014, Fuegen, Austria
- Pichler W, **Stratev D** et al. (2014) Influence of different process parameters on off-gasing and energy efficiency in wood pellet production, 10.2014, Pellet Industry Forum, Berlin, Germany
- **Stratev D** et al. (2015) From model rooms towards a modelled indoor environment, COST Action FP1303 Performance of bio-based building materials, 07-08.10.2015, Llandudno, Wales, UK
- Weigl M, **Stratev D** et al. (2016), Wood borne emissions in a real room environment – a modelling approach. WCTE 2016, World Conference on Timber Engineering, 10.2016, Vienna, Austria

Appendix I Supplementary data and supporting information

The following chapters reveal and discuss supplemental data from numerous experiments that are not presented in the publications cited above but are considered relevant by the author for a better understanding of the IAQ issues.

It should be explicitly pointed out that the majority of the author's experiments were conducted by using non accredited small-scaled equipment for scientific purposes (9.4) which results were proven to deviate from larger-scaled accredited equipment (unpublished results). Therefore in these occasions the reference to absolute indoor concentrations was avoided on purpose.

7. Historical overview - development of the VOC-related issue in Europe

An extensive graphical representation of the development of the VOC-related theme in Europe was given by Kuebart (Kuebart 2014). A comparatively thorough description of the depicted processes was given in (ECA-IAQ 2005). A shorter version of the story will be presented in the following paragraph (and visualized in Figure 2).

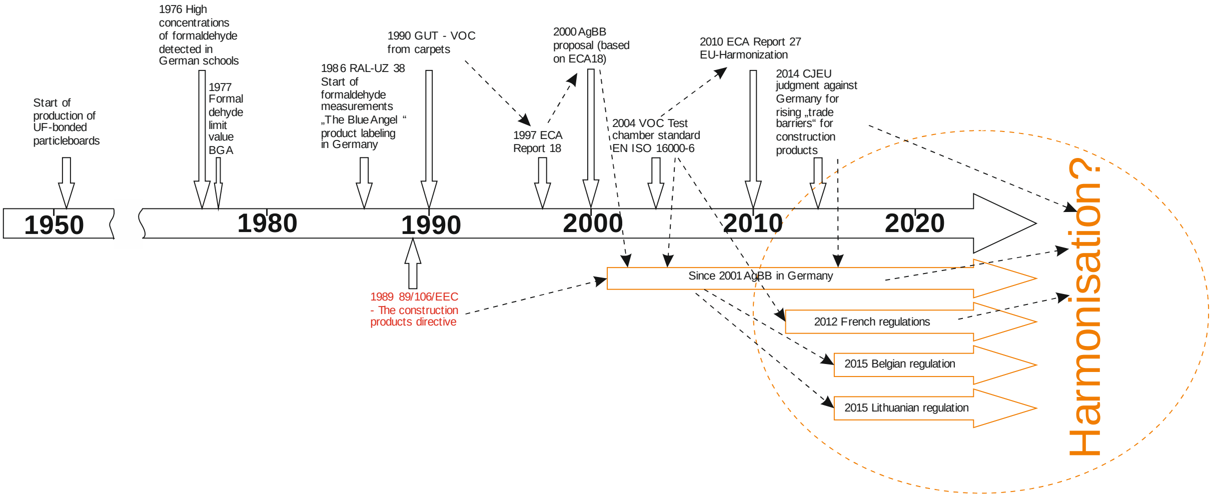

Figure 2. Development of the VOC-related regulations in Europe

The industrial particle-boards production by using urea-formaldehyde resin as an adhesive started in the early fifties of the 20th century. In 1976 the public interest towards indoor emissions was provoked by the fact that in some German schools in which particle boards were used as construction materials high formaldehyde concentrations were detected. In 1977, an ad-hoc group convened by the Federal Health Office of Germany (Bundesgesundheitsamt or BGA) proposed a maximum indoor benchmark value of 0.1 ppm for formaldehyde. As a consequence, a new guideline was issued and particleboards were classified into three categories according to their formaldehyde emissions. At first a large (40 m³) test chamber was supposed to be used for determining the so-called equilibrium concentration and was defined to be a reference testing method. However (this test was too extensive and) the industry demanded for more simple and faster correlating methods, like the "perforator" (EN 120) or the gas analysis (DIN 52368) method.

In 1990 the European carpet industry created the GUT-label (GUT in German stays for Association of Environmentally Friendly Carpets) and started monitoring the VOC emissions of the produced carpets in order to comply with internally set “environmental criteria”. For the period 1990-2004 the GUT label regulated the emissions of 4 individual substances and 2 summarized VOC indicators. Generally, the threshold values were lowered with each new draft of the GUT-label (Figure 3).

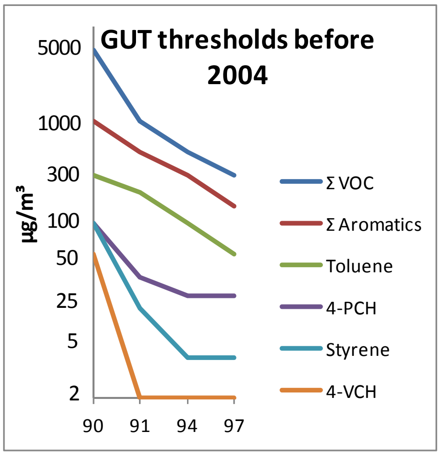

Figure 3. GUT limit values before 2004 (measured 24h after the start of the chamber test)

In 1997 the European Collaborative Action Indoor Air Quality and its Impact on Man (ECA-IAQ) published its Report No. 18 (ECA-IAQ 1997a) which proposed an elaborated labeling system with focus on flooring materials. The evaluation method described in the report’s proposal was supposed to be applicable to other solid surface materials through adaptation of the so-called loading factors and area specific ventilation rates. The intention was to provide a science-based and harmonized “evaluation starting point” for the European countries which was supposed to be implemented at national level. It should be pointed out that the penetration of the philosophy of ECA Report 18 at national levels was supported by the fact that some of the experts which drew up the draft of the proposal were also active experts at national level and could have direct influence on the changes in the environmental-related regulations in their own countries.

Since part of the principles of ECA-IAQ Report No. 18 have been implemented in the mandatory and volunteer regulations of several European countries and at the moment of writing of this work some of them are expected to be also implemented in the harmonized European regulations it is of importance to try to describe them. The objectives and philosophy of ECA-IAQ Report No. 18 were:

- Minimizing the risk from sensory irritation of the occupants after the third day of exposition through sensory panel (consisting of 10-15 members). Minimizing the risk of exposure of the panel members to volatile carcinogenic compounds through a preceding GC/MS measurement 24h after the start of the chamber test;
- Minimizing the risks of sensory irritation, odor nuisance and to some extend acute intoxication through introduction of the TVOC cumulative parameter (ECA-IAQ 1997b) determined through a GC/MS-VOC-measurement at the third day of the chamber test;
- Minimizing the risks of chronic intoxication through VOC measurement at day 28 after exposition start and through:
    - Assuming measured concentrations at day 28 for being long-run steady state concentrations;
    - Assuming that the emitted VOC belonging to a predefined list (so called relevant compounds) independently of their structure have additive negative effect on the occupants’ health proportional to their concentrations;
    - Assuming that the emitted VOC which are not included in the (relevant compounds’) list could have much higher negative effect on occupants’ health and their total concentration should not exceed 20 µg/m³;
- Minimizing the risk from life time exposure of the occupants to volatile carcinogenic compounds (to less than 10^{-5});
- Minimizing the risk of odor rejection by odor-sensible occupants through odor classification of the emissions at day 28 by conducting a panel test which should include ranking of the following characteristics:
    - strength of odor perception (if any)
    - degree of dissatisfaction with the odor characteristics

The proposal containing in ECA-report 18 was never implemented in its full extend most probably because of the following reasons:

- The complete testing procedure would be very time and costs extensive;

- The limit VOC concentrations would have been too restrictive (Stratev et al. 2016a);
- The subjective factors (panel tests) could have had unpredictable impact on industry.

In 1997 a workgroup of several German institutions (LAUG, AOLG, DIBt, ARGEBAU ect.) created AgBB (AgBB stays for Committee for Health-related Evaluation of Building Products). In 2001 the first draft of the so-called AgBB scheme was published. The introduction of AgBB accounted for the German implementation of the European Construction Products Directive 89/106/EEC (European Commission 1989). The first draft of AgBB was a stripped-down version of the ECA-report 18.

After a hearing with manufacturers and publishing a modified draft in 2002 a 2-year introductory test period was started. After a second hearing in 2004 the AgBB scheme was accepted by the representatives of the German manufacturers and state regulatory bodies (called stakeholders). In 2004, the German Institute for Structural Engineering (DIBt) took the AgBB scheme (DIBt 2004) as basis for developing the "approval principles for health-evaluation of indoor construction products". These were significantly relevant for gaining the Ü mark within the frame of the national technical approval and for the period 2004-2010 DIBt has issued about 350 approvals covering more than two thousand products (DIBt 2010). DIBt has only considered floor coverings, adhesives and coatings for parquets and wooden floorings (named as "Lacquers" in the figure). It was supposed that further products (like adhesives for all floor coverings wall coverings, underlay areas for sport halls and suspended ceilings Internal partition kits) would also be controlled by DIBt (DIBt 2010).

Non-mandatory approaches similar to the procedures described in ECA report 18 and the AgBB scheme have been proposed by CSTB in France (AFFSET) by LQAI in Portugal, by the Austrian Ecolabel. Though most of the European indoor labeling schemes were voluntary, they have reached high market coverage. Well-known systems established in Germany but now in use in several European countries apply to emissions of adhesives and other products for the installation of floor coverings (EMICODE), and carpets (GuT). Despite their private status, these product labels (for example EMICODE) have up to 80% market coverage in Germany (ECA-IAQ 2005) and the use of their assessment is becoming more and more popular in other European countries like the Netherlands, Sweden, Austria, Switzerland, and in the United Kingdom. Other important labeling schemes (which could be regarded as derivatives to AgBB) with high market coverage in the so called D-A-CH region (Germany, Austria and Switzerland) are The Blue Angel (RAL gGmbH), Sentinel Haus, Baubook, Natureplus etc.

In 2015 another two European countries (Lithuania and Belgium) introduced mandatory labeling schemes for controlling the indoor emissions of the building products.

In its structure the Lithuanian scheme (MH of Lithuania) is similar to the AgBB but there are some relevant differences regarding the calculation of the so called R value an in the LCI concentrations (Stratev et al. 2016a).

Undoubtedly the development of the IAQ theme in Europe was very dynamic especially in the last decade. The consumer demand towards products with better characteristics regarding VOC emissions was also raised. Unfortunately, this was done at the cost of regional fragmentation of the evaluation schemes which led to supplemental burdens for the producers in order their products to be tested and approved for the regional markets. The current situation is especially discriminating for the smaller producers who in the majority of the cases are not able to bear the costs for testing according all effective schemes and thus could not achieve their sales potential. Seeing that the integrity of the inner-European market for construction products is under threat the European Commission tried to interfere and to turn around the course of fragmentation. The European Commission brought a legal action against Germany for raising "barriers to trade" with its rules and practices concerning the Ü mark for approval of construction products. In October 2014 the European Court of Justice (ECJ) ruled that through the use of what are known as Building Rules lists (Bauregellisten) the Federal Republic of Germany had impeded market access to Germany for construction products already carrying CE conformity marking (European Court of Justice, of 10/16/2014). The court confirmed that it is not allowed to establish a national approval system for properties of products that are dealt with in CE marking and the related harmonized EN standard. As a result DIBt considered to stop the national technical approvals of construction products beginning with 2016, and to substitute these with requirements on the construction work (Eurofins 2015).

The decision of ECJ should not be interpreted as the end of the IAQ regulations on construction products in Europe. It only points the direction towards harmonization of the fragmented regulations and the emergence of a unified European scheme for evaluation of construction products with respect to IAQ. Such scheme is in its final stage of development.

It is very important to be pointed out that almost all VOC schemata in Europe are based on the ISO 16000-9 analytics. However, some of them (like AgBB for example) acknowledge only the results of preselected analytical laboratories and do not automatically accept results from all accredited ISO 16000-9 certified labs. Other important limitations of the schemata are the strong requirements in respect to the loading factors and air exchange rates applied for the tests. The author’s opinion is that these constrains should be loosened to some extend and the theoretical concentrations (or emissions) should be mathematically derived from the determined area specific emission rates. In this way, it would be possible combined tests like for example ISO 16000 and EN 717-1 to be carried out. Thus the costs which the companies bear for certification of their products can be reduced.

A relatively new European standard for assessment of release of dangerous substances (DIN CEN/TS 16516) paves the way in this direction (paragraph 7.3 of the standard) by allowing deviations from the calculated loading factors (paragraph 4.2.2 of the standard) from 50% to 200%. However the selected limits allow combined method measurement with EN 717-1 only for products with target loading factors of 0.5 to 2.0 m^2/m^3 like for example wall panels.

8. Evaluation

8.1. Exposure assessment of indoor air pollutants

Extensive reviews on the assessment approaches for VOC in Germany are done by the Association of Ecological Research Institutes (AGÖF) (AGÖF 2013a) and by Heinzow and Sagunski (Heinzow, Sagunski 2009). The author of this work to a great extend agrees with the conclusions and the proposals made in the pointed papers and the next paragraph is citing most of them, however some additions and changes will be proposed.

According the authors above there are two types of VOC - assessment guidelines that have become prevalent:

- Statistically derived assessment concepts
- Toxicologically derived assessment concepts

Both assessment concepts are based on conventions, which are meant to reflect **a scientific sociopolitical consensus** (AGÖF 2013a).

Toxicologically derived assessments result in guideline values (like for example NOAEL) that are supposed to answer health-related questions. These values originate from experiments with laboratory animals which are exposed to different concentration levels of a compound or are based on observations from occupational studies, in which employees are exposed to high concentrations of the compound (as a result of their occupational activity). In order to protect susceptible population groups (infants, sick people), so-called uncertainty factors are applied additionally. With this approach, it remains open to what extent nonspecific health symptoms such as headaches, concentration problems, etc. can be recognized. Nonspecific symptoms are the most frequently mentioned health problems in the context of indoor air quality. Furthermore, indoor air usually contains compound mixtures that cannot be evaluated by toxicological reasoning and the introduction of uncertainty factors, e.g. a **factor of one hundred**, cannot be justified by toxicological reasoning and **is based on conventions** (AGÖF 2013a). The toxicologically derived assessment has the following important drawbacks:

- High cost of generating toxicological data and thus a small number of guideline values available;
- This approach is not adequate for establishing verified assessments for mixtures of all possible chemical compounds occurring in indoor air.

In the statistically derived assessment concept, reference values are developed. From a large number of representative investigations, a "usual, average" level of indoor air pollutants is established and defined as "normal." In many cases, the so-called 90th or 95th percentile is chosen as the concentration threshold, whereby any value exceeding the latter indicates an unusual exposure (AGÖF 2013a).

Based on the available frequency distribution, AGÖF sets the 90th percentile of the measurement values for event-specific data as the upper reference value because this can be interpreted as the upper limit of the background level deemed as safe.

The statistically derived assessment has the following weak spots:

- A much broader database set is necessary for deriving representative results hence it could be expensive;
- It does not represent adequately the introduction of new chemical compounds or compound groups released into indoor air (like for example by the introduction of a new production process) as no reference values will be available at first;
- In the event of an increased application of known compound groups due to a change in production (e.g. when solvents in paints were replaced), established reference values can also consistently be exceeded;
- *It is geographically (market) constrained and depends on the predominating consumer behavior and on the industrial production for the corresponding geographical region;*
- *It does not represent adequately the concentration distributions in the "low concentrations" range especially for non ubiquitous compounds;*
- *Statistically derived assessment almost never includes supplemental information about nonspecific symptoms and thus the relation between VOC* distribution and nonspecific problems could be hardly derived.*

Only by considering statistical relationships combined with toxicological data *as well as information about the specific and nonspecific symptoms*, health risks can be weighted and the sources of indoor air problems identified.

Additional generalistic guidelines or assessment tools such as the R-concept or the TVOC concept could be useful for the consumer's decision making or for granting market access for the product but it should be pointed out, that product classifications according these concepts do not necessarily correlate with the true health risks. Thus it is responsibility of the institutions approving such concepts to do their best in order to avoid unfounded restrictions towards certain product groups. Such aspiration (at least for the R-concept assessment) is visible when the historical development of AgBB is examined. The updates in some LCI-values with the new iterations of the AgBB-scheme have impact on the level of the R-value assessment and according the author represent an effort to address certain non-uniformities in the early versions of AgBB. However it remains open whether such changes should be made at the level of LCI instead to directly change the R- or the TVOC- limit for certain product groups based on natural materials like softwood for example.

Odor problems, on the other side, are not satisfactorily addressed by the assessment apparatus described above (Thumulla et al. 2016). Additionally some odor-relevant-compounds in their usual indoor concentrations are not even detectable when using Tenax™/TD/GS-MS analytics. Thus the odor theme in the IAQ-assessment remains unsatisfactorily covered and is expected to be a major research topic in the next decade(s).

8.2. Evaluation of IAQ assessment schemata

The impact of IAQ-assessment schemata should also be evaluated. At first it is of interest whether they achieve their goal to predict the real indoor concentrations. More generally it is from interest whether the appliance of the schemata leads to a better indoor air quality. Not at least it is important to know what the restrictiveness of IAQ schemata towards industrial production is.

8.2.1. Evaluation of the prediction accuracy

If analytical uncertainty is neglected there are two types of methodology deviations which could be of interest when considering IAQ evaluation schemes.

- Deviation of the determined VOC* chamber concentrations at day 3 and 28 from the concentrations determined in the real (or model) room.

- Deviation of the VOC* concentrations at day 28 (if any) from the “long term” concentrations.

In other words, it is of interest whether the measured VOC* concentrations in the test chamber at day 3 and 28 correspond with the reality and whether the choice of day 28 as indicator for the long-term exposure is justified.

Another relevant question is whether the deviations (if any) are dependent on the type of the construction material used.

The author took part in researches covering all three topics (Höllbacher et al. 2015)(Stratev et al. 2015a).

An important milestone of the first project (Höllbacher et al. 2015) was the comparability in the measured concentrations at day 28 for ISO 16000-9 test chamber and DIN CEN/TS 16516 model room to be verified. Two model rooms were built up as the materials of choice were OSB and CLT. Samples from these materials were also measured in two 225 l emissions test chambers according ISO 16000-9. The values of the relevant parameters for the experiment are given in Table 2.

Table 2: Relevant parameters of the experiment (Höllbacher et al. 2015)

Parameter	Values			
	Model rooms		Test chambers	
	CLT	OSB	CLT	OSB
Chamber volume [m^3]	30	30	0.225	0.225
Air exchange rate [1/h]	0.5	0.5	0.5	0.5
Air flow [m^3/h]	15	15	0.113	0.113
Exposed area [m^2]	55.3	55.3	0.400	0.360
Loading factor [m^2/m^3]	1.84	1.84	1.778	1.600
Area specific air exchange rate - q [$m^3/(m^2.h)$]	0.271	0.271	0.281	0.314
Panel thickness [mm]	97	22	97	22

The results (Figure 4) show that the evaluation at day 28 according to ISO 16000-9 leads to overestimation of the TVOC concentrations in the indoor air for both materials with a factor of approximately three when compared with the TVOC concentration in the model rooms. The small differences in the area specific air exchange rates (Table 2) cannot be the reason for the observed deviations in the measured concentrations. An attempt to explain the discrepancy between the results is done in 9.3.

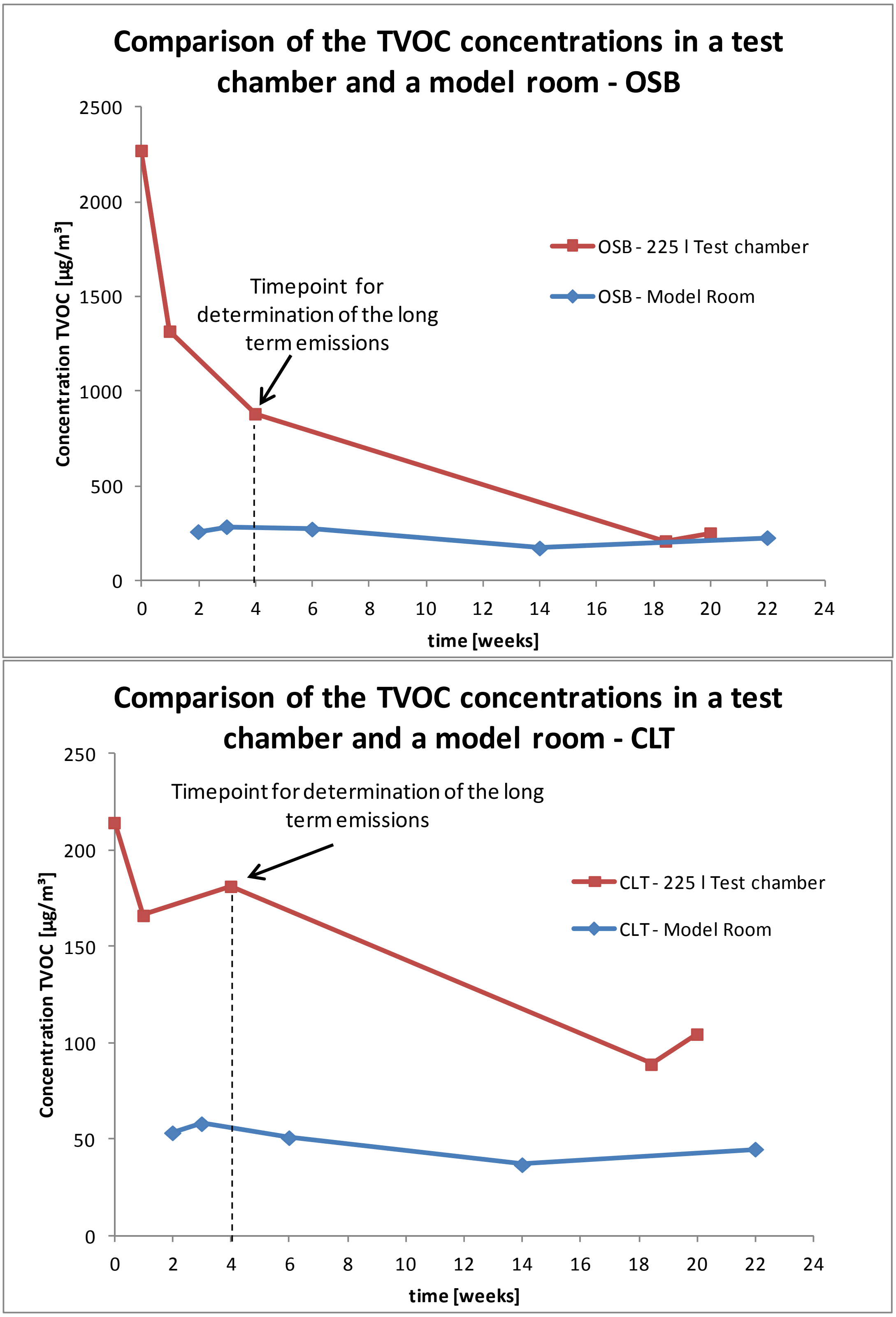

Figure 4. Comparison of TVOC concentrations in 0,225 m³ chambers and 30 m³ model rooms

In the second research (Stratev et al. 2015a) construction materials on pine-wood basis have been chosen (OSB, CLT, OSB/GKF, clay covering timber shell) and were compared with construction materials on inorganic basis (steel and steel/clay combination). One of the tasks of the experiment was to determine whether the emission levels at day 28 were stable (steady state) over the following time period or whether there was a significant emissions decline after day 28. The relative decline of the emissions for a certain time period after day 28 would be equal to the methodological safety margin (for the tested material). The IAQ-relevant parameters of the experiment are given in Table 3.

Table 3: Characteristic parameters of the tested model rooms

Object*	Material	Volume	Ventilation	T, RH%*
MR_1	OSB*	30 m^3	0.5 h^{-1}	23°C, 50%
MR_2	GKF/OSB*	30 m^3	0.5 h^{-1}	23°C, 50%
C_1	CLT*	69 m^3	0.4 h^{-1} **	~22°C
C_2	Clay/Timber shell	69 m^3	0.4 h^{-1} **	~22°C
C_3	Clay/Steel shell	68 m^3	manual	~22°C
C_4	Steel	68 m^3	manual	~22°C

* MR_i- model rooms; C_i - office containers; T - temperature; RH% - relative humidity; OSB - oriented strand board; GKF/OSB - gypsum fibreboard in an OSB shell; CLT - cross laminated timber;

** Basic setting: Automatic ventilation with control system based on CO_2-concentrations.

Table 4. Long run (assessment) concentration safety margins

Model room or container	VOC	Safety margin for the period of the experiment					**6 M safety margin**	**12 M safety margin**
		measured	model$_{w.d.}$	model$_{28}$	error model$_{28}$	period [months]		
MR_1-OSB	TVOC	3.3	2.8	3.1	3%	8.3	**2.4**	**3.4**
	Pentanal	3.7	3.6	4.5	23%	8.3	**3.0**	**4.5**
	Hexanal	5.2	4.1	4.6	0%	8.3	**3.3**	**5.2**
	α-Pinene	3.1	2.5	2.6	-9%	8.3	**2.2**	**3.0**
MR_2-GKF/OSB	TVOC	1.7	1.5	1.6	0%	4.5	**1.7**	**2.1**
	Hexanal	1.7	3.6	4.4	68%	4.5	**4.5**	**8.1**
	α-Pinene	1.3	1.6	1.6	13%	4.5	**1.7**	**2.2**
C_1-CLT	TVOC	21.3	19.6	14.4	-30%	20.8	**5.3**	**11.0**
	α-Pinene	37.7	38.2	34.4	-9%	20.8	**5.9**	**16.7**
C_2-Clay/Timber	TVOC	7.8	5.7	14.9	121%	20.7	**2.3**	**3.7**
	α-Pinene	50.3	48.0	56.5	15%	20.7	**7.4**	**21.1**
C_3-Clay/Steel	TVOC	no safety margins detected						
C_4-Steel	TVOC							

The results from this research (Table 4) showed that the constructions based on softwood materials did not reach steady state condition of their indoor VOC emissions within the 28 days' timeframe (specified in the majority of the current IAQ evaluation schemes). The measured safety margins for the 6- and 12- month periods for softwood construction materials varied between 1.7 and 21. On the other hand no safety margins were detected for constructions based on inorganic materials.

Both results indicate that the evaluation of softwood products according ISO 16000-9 does not always reveal the real scenario concentrations and there is a big chance for overestimation hence for categorizing products on softwood basis as lower level products than they really are. The results also indicate that further research in this direction is needed in order more precise predictions to be possible.

8.2.2. Evaluation of the positive effect of IAQ schemata

The effect of the regulative schemata on the improvement of the IAQ should be undoubtedly positive and was previously discussed (Rehwagen et al. 2003) (Ahrens et al. 2007) (Wilke 2013) and (AGÖF 2013b) . However there are several sources of uncertainty which deserve to be topics of further research: At first it is difficult to prove statistically significant reduction because a long time period should be monitored and an adequate number of measurements should be conducted before and after the change of the threshold concentration. An expected occurrence which can be observed after tightening the threshold concentrations for certain substances is that industry adapts its production in order to reduce the emissions maximum by using scavengers or antioxidants or in favor of emissions of new and non-regulated substances or such which are hardly detectable (10.1). The changes in consumer behavior should also be considered when evaluating the effectiveness of IAQ schemata and Figure 5 (Ahrens et al. 2007) is a good example for that. It is visible that for the period 1985-2007 a reduction of the indoor concentrations of halogenated hydrocarbons (which are typical for the polymer industry) is observed. In contrast the concentrations of alpha-pinene (which is indicator for the usage of softwood based products) increased approximately five times. Thus, the reduction of halogenated hydrocarbons could be correlated with both tightening the emission regulations (with respect to halogenated hydrocarbons) and the shift of consumer's preference towards interior products based on softwood materials. It is however impossible (when only considering Figure 5) to quantify the influence of each factor.

As a result of tightening threshold concentrations the social perception for certain products emitting the substances at levels close (but not necessarily above) the LCI values suddenly ranks them as "more harmful" as before. The changes in social acceptance will have impact on the consumer behavior. In this aspect it should not be forgotten that the current evaluation schemes are meant to reflect a scientific sociopolitical consensus (8.1) and the usage of mathematical methods for comparing of threshold levels and emission levels does not necessarily reveal the differences in the health hazards related to the products.

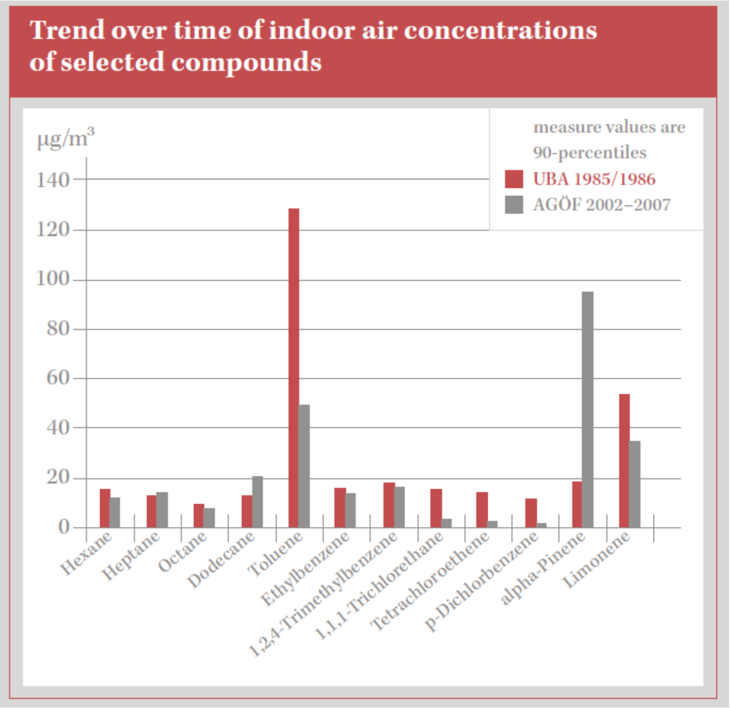

Figure 5. Example for shift in concentrations of certain pollutants of concern over the 20 years period (Ahrens et al. 2007)

8.2.3. Evaluation of the effect of IAQ schemata on industry

At present there are more than ten different VOC (mandatory and voluntary) VOC evaluation schemes with high market coverage and high influence on industrial production in Europe (7). Every several years the existing schemes are being updated or new ones appear. Slowly it becomes hard even for testing facilities to comply and to take into consideration all the rules and important details of the IAQ evaluation schemes. In order the industry to also have the chance to assimilate the changes (before or as soon as possible after they occur) it should have fast and effective tool for aligning and comparing its production characteristics with the new rules.

A methodology for numerical evaluation of IAQ schemes containing LCI list has been proposed by the author (Stratev et al. 2015a). The idea behind it is to calculate the possibility of a certain production (based on statistical data of its emission properties) to emit certain substances above their threshold levels (LCI) set in the evaluation schemes. This possibility could be also called discrimination of the evaluation scheme towards the production of interest. It should be considered that the calculated discrimination by applying the rules in the cited paper is only partial because there are also other rules in the evaluating schemes than just comparing the emitted substances against a list of threshold concentrations. These rules could be further implemented after careful mathematical translation of their impact by the evaluation.

In the methodology proposed by the author (Stratev et al. 2015a) the partial discriminations of ECA-IAQ Report 18 and AgBB drafts from 2002 to 2015 as well as Lithuanian IAQ evaluation scheme against a hypothetical representative industrial product for indoor use were calculated. The VOC* characteristics of this hypothetical product were derived from data published from the Association of Ecological Research Institutes e.V (AGÖF 2013a) and the average distribution function of the (normalized) VOC concentrations was derived from another AGÖF publication (Hofmann, Plieninger 2008). Based on the average cumulative distribution a mean probability function of the VOC concentrations of the hypothetical representative indoor related product was derived (Figure 6). It should be pointed out that the potential form of describing real life distribution of chemical concentrations is not the most suitable one (US-EPA 2001) and in a further refined edition of the methodology another regression model could be considered.

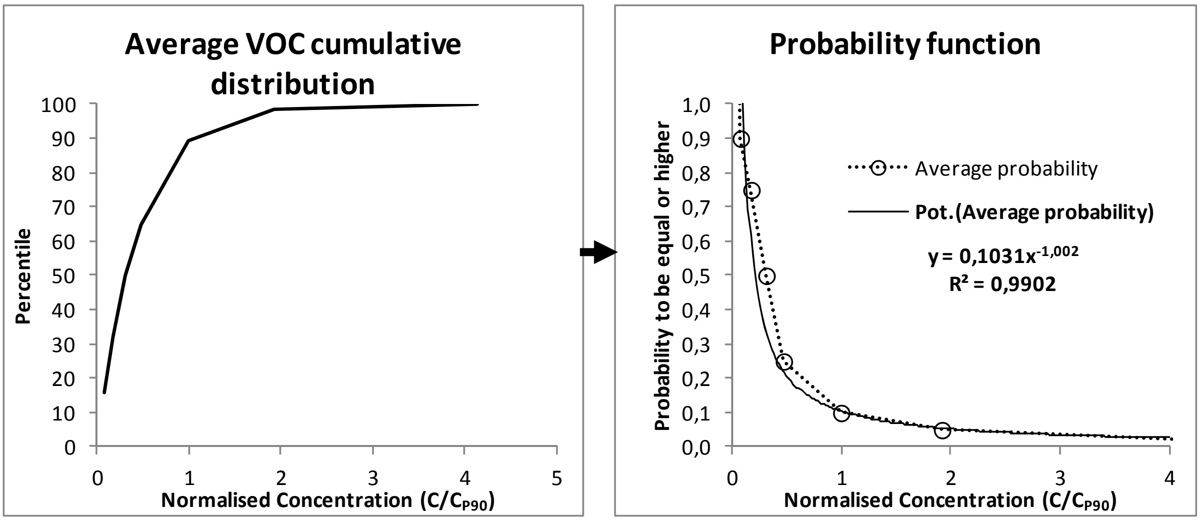

Figure 6. Deriving a mean probability function of the VOC concentrations of the average indoor related product

9. VOC* emissions from softwood based panels and their measurement

9.1. Primary and secondary VOC

Depending on their formation VOC* could be separated into two groups: Primary VOC are those organic volatiles which are present in the product's material(s) (in their volatile form) before (or when) the product was created and are not formed as a result of chemical decomposition during the storage or usage phase of the product's lifecycle. Primary VOC* which are characteristic for softwood based panels are terpenoids or not completely cross-linked formaldehyde of the resin mixture for example.

Secondary VOC* are built during the chemical decomposition of bigger "non-volatile" molecules as a result of their oxidation or hydrolysis. Secondary VOC are aldehydes which are formed after oxidation and decomposition of unsaturated fatty acids (Belitz et al. 2008), hydrolyzed acetic acid from the hemicelluloses (Keey et al. 2000), furfural or hydrolyzed cross-linked formaldehyde from the UF-resin.

The VOC* separation in such subgroups makes sense when the emission rates versus time functions are to be characterized. If the climatic conditions are kept constant (like in a VOC test chamber) primary VOC exhibit typical decay form of their emission rates versus time functions. The form of the functions for the secondary VOC is dependent on the effective conditions in the periods preceding and during the test phase.

Examples for the behavior of primary and secondary emissions from softwood-based panels are given by Makowski, Ohlmeyer et al. (Makowski et al. 2005; Makowski, Ohlmeyer 2006a, 2006b) and on Figure 7.

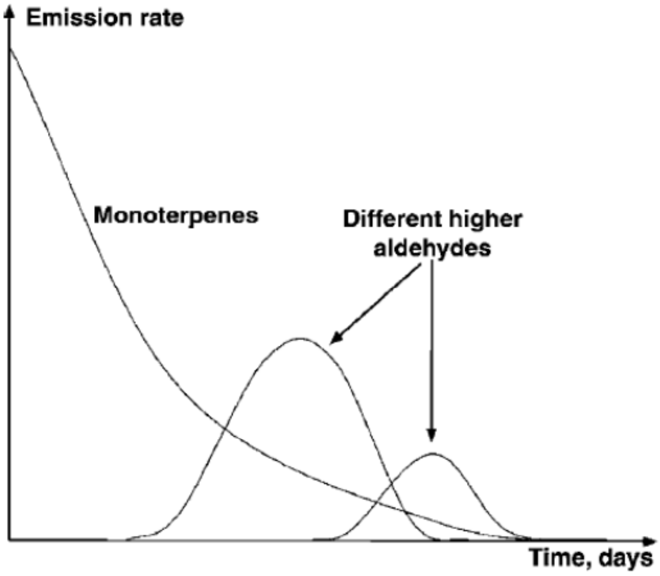

Figure 7. Expected (primary and secondary) VOC emission rates versus time from softwood-based panels (Makowski et al. 2005)

9.2. Instrumental analysis of VVOC VOC and SVOC

The concept of IAQ evaluation in the European schemata was originally developed around analysis based on sorptive pre-concentration (on Tenax™) followed by (qualitative and quantitative) gas chromatographic determination (ISO 16000-6:2004). This combination of analytical steps is very suitable for detection of VOC and SVOC but much less suitable for VVOC. VVOC don't tend to bind good on the chosen sorbent (Tenax™) and often are eluted very early by the chromatography (with the air or the water peak). Because of these technical difficulties VVOC were initially not of concern in European IAQ evaluation schemes (with some exceptions like formaldehyde). The last was usually detected photometrically by using the so called acetyl acetone method (DIN EN 717-1). A major disadvantage of the acetyl acetone method is that it is not convenient for samplings outside of the testing laboratory. The introduction of the DNPH analytical method which is suited for very volatile carbonyl compounds (DIN ISO 16000-3) expanded the possibilities for easy and cost effective analysis with on-site sampling and led to the inclusion of several very volatile carbonyl compounds in the current AgBB draft (UBA Deutschland).

The author was involved in both sorption-TD-GC/MS and DNPH-HPLC-UV detection techniques and in the following paragraphs will follow some conclusions based on his experience.

9.2.1. Sorptive and thermal desorptive - GC/MS/FID analysis

The sorptive and the thermal desorptive GC/MS analysis of VOC and SVOC from softwood based products is not a challenge on a dedicated analytical GC/MS system with a suitable GC-column. It is much more challenging when trying to sustain stable analytics on a non-dedicated system (which is also used for other type of analysis) in order to avoid constant recalibrations or when using FID as a detector.

Important requirements for the accurate VOC* identification are:

- Knowledge over the properties of the chromatographic column in use;
- MS-database containing high quality spectra of the eluting compounds;
- High enough SNR ratio.

The chemical structure of stationary phase of a chromatographic column determines its polarity and the strength of the interaction with the analytes. The strength of the stationary phase - analytes interaction and the analyte's volatility determine the sequence in which a mixture of analytes will be eluted when separated on the column of interest. As mentioned in 1.1 the retention indices can be used as qualifiers in cases where no other qualitative information is available.

During his work with the HP Pona chromatographic column (Agilent 19091S 50 m x 0.2 mm i.d. x 0.5µm by using a temperature ramp program) the author was able to determine the retention indices of more than 100 VOC and the majority of them can be related to softwood products (11, Table 10). Under consideration of Table 10 it is clear that the determination (separation) of the red marked VOC would be problematic if only FID is used as a detector. This is due to the fact that compounds with differences in their RIs equal or smaller than five are usually not baseline separated on the above-mentioned HP Pona column hence not easily quantifiable.

Retention indexes are critical not only for FID-based detections but also for MS-based identifications in the cases where SNR is low (like by low concentrated VOC). In these cases, the quality of the mass spectra is not high enough for clear identification of the eluting compounds and RIs could be used as supplemental identifiers.

Not at least RIs could be also used in scenarios where MS analytics with high SNR is used but no MS-database is available. In these cases with the help of public available databases (NIST Mass Spec Data Center; NIST Mass Spec Data Center') and/or chemical structure analysis software (NIST) a material specific MS-database could be created if the MS software supports this feature (like Agilent MSD-Chemstation).

Special attention should be given to the detection of aliphatic carboxylic acids on apolar column by means of GC/MS. There are two major hindrances which should be taken into account:

- The shape of the peaks (Figure 36) does not resemble to the regular (Gaussian) curve;
- The MS-response is not stable and is very dependable on the purity of the ion source and the autotune-parameters. Therefore, for optimal quantification a dedicated IST (carboxylic acid) should be used.

9.2.2. DNPH-HPLC analysis of very volatile carbonyl compounds

The DNPH-HPLC analysis is a comparatively new routine method which is in a very good agreement with the classical Hantzsch formaldehyde detection (Giesen et al. 2016). Furthermore not only formaldehyde but also other very volatile aldehydes and ketones can be analyzed by means of DNPH analysis. The theory of this type of analysis is extensively described in the corresponding standard (DIN ISO 16000-3). However, because the practical application could leave some questions open the author describes a tested working scheme of equipment and testing parameters which could deliver reliable results.

The sampling could take place on BPE-DNPH cartridges (Sigma 54278-U or 54279-U) with 1,1 l/min till approximately 80-100 liters of air are collected. A membrane pump (like KNF LABOPORT® N 86 KN.18 PPS 2) could be used for the parallel sampling of two samples. Two mass flow controllers with totalizer (like for example the Vögtlin SMART GSC-B5TA-BB26 or the manual red-y compact 2 series) could be used for adjustment of the flow rate during sampling and for measurement of the total sampling volume. PFTFE tubing with luer-to-tubing connectors (like Sigma Z101168-4EA) are suitable for attaching the cartridges to the sampling system.

In September 2014, the author and his team took place in a round robin test for formaldehyde, acetaldehyde, butyralaldehyde, propionaldehyde ("Ringversuch Aldehyde 2014" / IFA der DGUV, Alte Heerstraße 111, 53757 Augustin) with more than 35 participating labs and completed it successfully with good z-scores. The following analytical system was used for the purpose:

- Column: Thermo Scientific Acclaim Carbonyl C18, 3 µm 120A 3,0 x 150 mm;
- Eluent: acetonitrile/30% Milli-Q-water V/V;
- Total volume of desorption: 5 ml;
- Injection volume: 8 µl;
- HPLC-System[3]: Thermo: LPG-3400SD pump with WP-3000SL autosampler and UV-VIS DAD-3000 detector;
- HPLC Solvent: acetonitrile/water (Milli-Q)

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[3] Could be each system with a gradient pump capable of sustaining stable 220 bar of pressure and with a sensible detector at approximately 360 nm

- Gradient/temperature program: 12 min isocratic at 53% ACN and 47% water, then linear to 100% ACN in 4,5 min and 3,5 min stay / T=const=28°C
- Flow-rate: 0,6 ml/min
- Detector‘s wavelength: 360 nm
- Consideration of the recovery rate: no

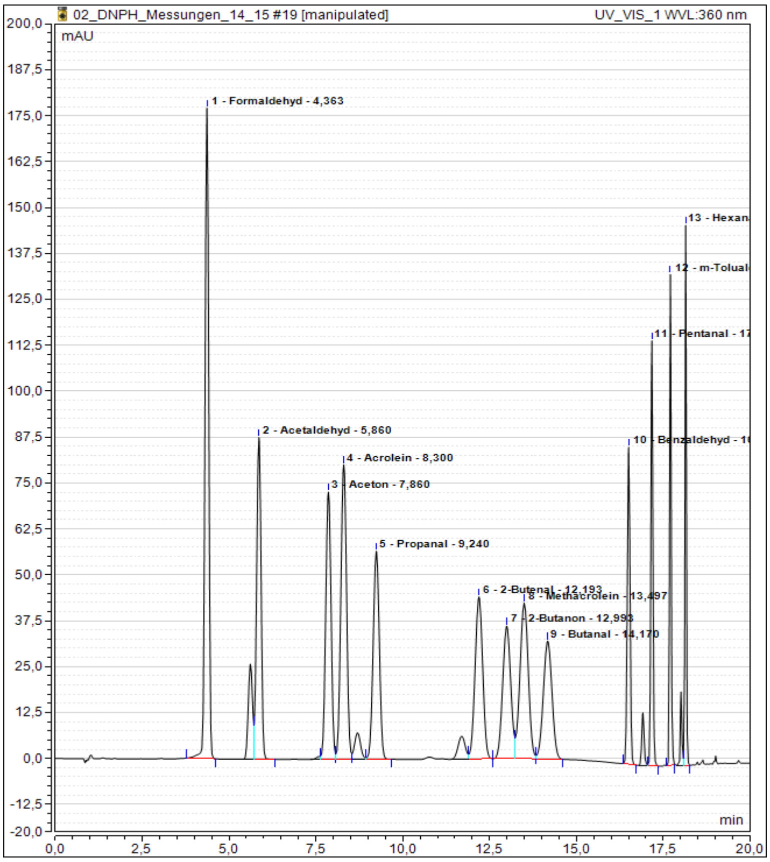


Figure 8. Separation of carbonyl-hydrazones containing in a diluted Sigma 47651-U standard on a Thermo Acclaim Carbonyl C18 column (3 µm 120A 3,0 x 150 mm) and by using acetonitrile/water gradient program

The HPLC system was calibrated for the range of approximately 15 - 600 µg/m³ by using Sigma 47651-U or/and CRM47651 standards. The separation of the Sigma standards on the Acclaim Carbonyl C18 column (Figure 8) was better than that described in the standard (DIN ISO 16000-3) method.

9.2.3. VOC sensors

Experiments conducted by the author (in 2013) aiming the appliance of metal oxide gas sensors for TVOC quantification revealed that this type of sensors was not reliable for quantitative analysis of VOC from softwood products (results not shown). An extensive review over the possibilities of using mobile sensors is done by (L. Spinelle et al. 2015).

9.3. Considerations about the test setups for VOC emissions evaluation and introduction of basic dynamic VOC emissions model

The purpose of this chapter is to comment some specific questions which are not discussed to the necessary extend in the IAQ evaluation schemes and testing standards. Because of this there are often different points of view how the testing procedure should be conducted. These differences could lead to great variations in the testing results generated from different laboratories even when specimens with identical VOC-related characteristics are being tested.

Figure 9 visualizes the path(s) of the VOC emissions generated from cross laminated timber used for the construction of flat roofs. There are two emission fluxes which could be considered to be relevant: The internal VOC emissions (IE) are of greatest interest, because in combination with the ventilation (air exchange rate) they directly affect the indoor VOC concentrations; External VOC emissions (EE) are normally not from interest for IAQ evaluating schemes, however their characterization is also important because they reduce the potential of the emitting object to generate IE. An analogy of VOC emissions with current flow from a battery through two parallel circuits is made in Figure 9c. Here the indoor emission rate could be compared to the intensity of the red light generated from the red bulb. The light intensity is measured with the help of a color selective detector. The detector’s color filter ensures that only “indoor” light intensity is to be measured.

There are several parameters which could influence this current (the bulbs are selected so that by equal other conditions the light intensity is also equal):

- Capacity and internal resistance of the battery (which have influence on the supply voltage);
- Resistance of the resistors (coating layers) - determines which of the two possible paths would be more conductive;
- Capacitance of the capacitors (internal coating layer) - could also temporarily affect the intensity of the red light (IE).

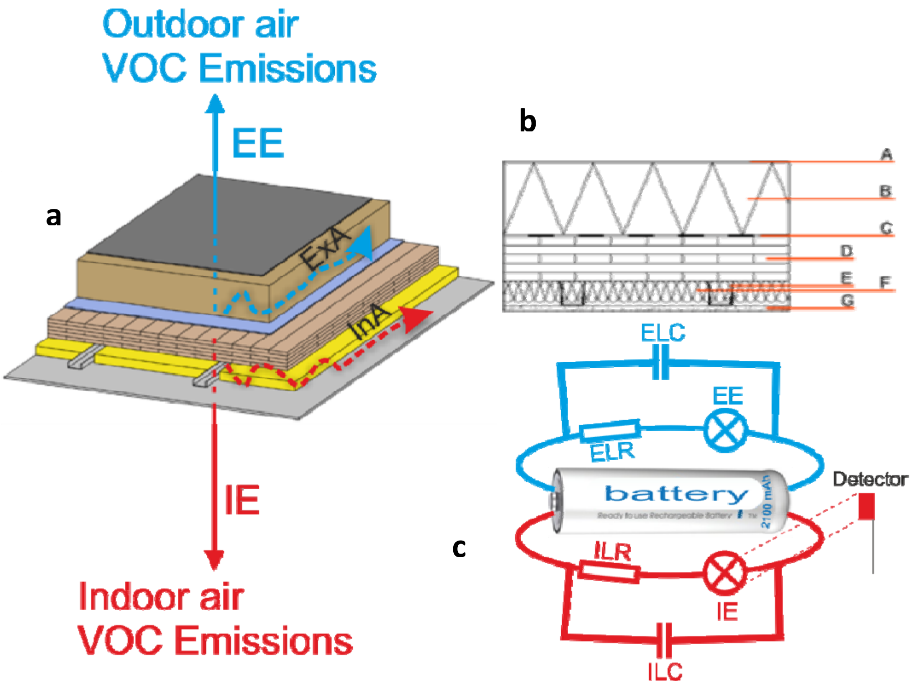


Figure 9. Scheme of wood VOC emissions from solid wood construction. a) and b): Flat roof (Holzforschung Austria 2015) EE – external emissions, ExA – external adsorption, IE – internal (indoor) emissions, InA internal adsorption, A - sealing sheet, B - insulation material, C - sealing sheet e.g. bitumen, D - cross laminated timber at least five layers, E - acoustic hanger, F - exchangeable layer, G - gypsum plaster/fiber- boards; c): Analogy of VOC emissions with current flow from a battery through two parallel circuits, battery (with certain voltage, capacity and internal resistance), ILR – internal layer resistance, ILC - internal layer capacity, IE – internal (indoor) emissions, ELR – external layer resistance, ELC – external layer capacity, EE – external (outdoor) emissions.

Usually emissions from construction materials like the CLT at Figure 9 are evaluated as cut-outs from the material of interest are tested partially sealed with low permeable aluminum tape. The most common practice is to seal the cutting edges and to leave both emitting surfaces free. This testing setup and its electrical circuit analogy are presented on Figure 10.

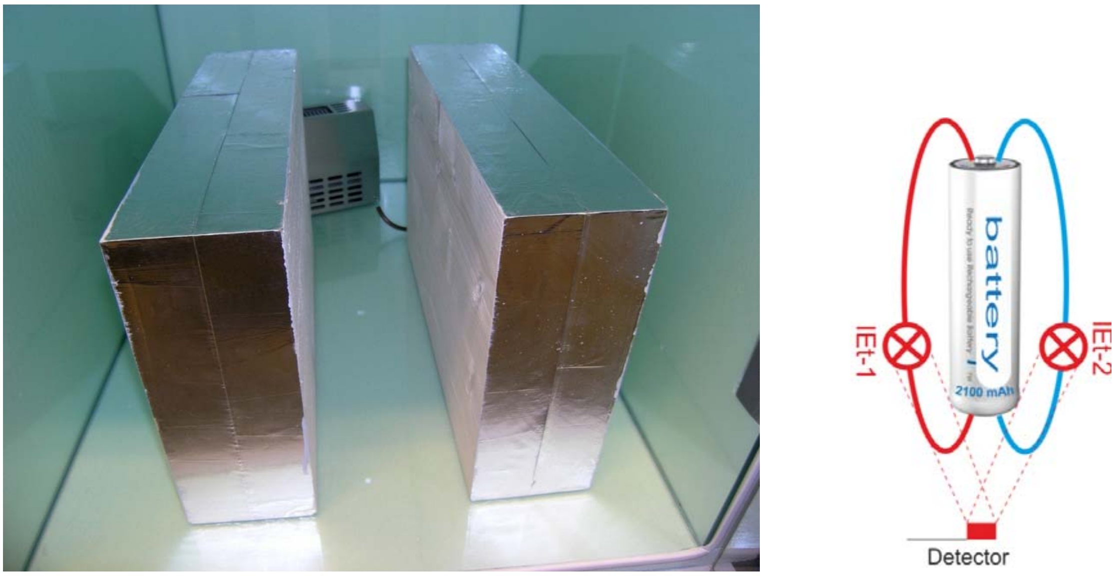


Figure 10. Scheme for VOC testing of CLT plates in a 225 l testing chamber with both emitting surfaces left unsealed

Another common practice is to completely seal one of the emitting surfaces and to leave the other one free (Figure 11).

Figure 11. Scheme for VOC testing of an acoustic plate in a 225 l testing chamber with one emitting surface left unsealed

The most “advanced” practice is to seal the back side and the edges of the test specimen with aluminum tape and to cover the emitting “front” side with the insulation materials used in the real scenario setup (Figure 12).

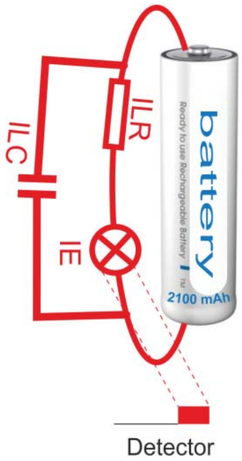


Figure 12. Schematic representation of testing VOC emissions from sample with sealed backside and covered with insulation layers

Another not so popular practice is to leave the cut surface (edges) of the test specimen unsealed. This could be problematic in cases where the VOC flux in in-plane direction (Figure 21) is much higher than the transverse flux (OSB) or is unusually increased because of scaling down VOC measurement setup (9.3.3).

One of the aims of the current paragraph was to visualize that neither of the commonly used VOC-emissions test setups depicted at Figure 10 through Figure 12 resembles the real situation (on Figure 9 left). The following chamber setup proposed by the author (Figure 13) in which the sample with its covering layers is put in a tunnel between two chambers most closely reproduces the real scenario.

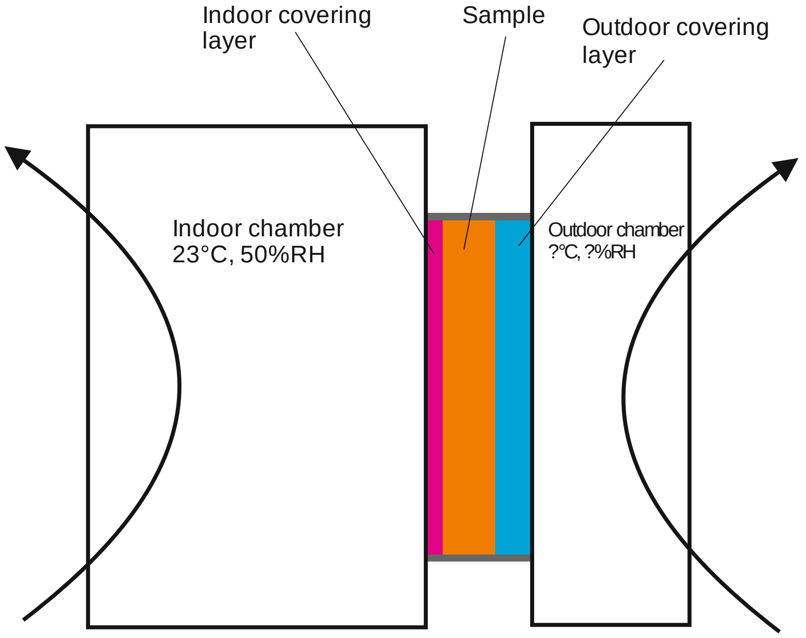


Figure 13. Close to reality VOC test chamber setup

9.3.1. Modeling of VOC mass transfer inside and outside the test specimen

If a wooden sample with (idealized) homogeneous structure is wrapped in a gas-tight packaging and stored for a long enough time period, the concentrations of a chemically stable, primary volatile compound (VOC_i) at each point within the sample volume will even out. If the impermeable packaging of the "top" side is then removed and the top sample surface is exposed to a clean, non-VOC_i-loaded air flow, a VOC_i flux (emission) from the sample volume (through the top sample surface) to the surrounding air will be observed (Figure 14). A VOC_i concentration redistribution inside the sample volume will also take place and if the sample structure in direction parallel to the top surface is isotropic the VOC_i flow vector, will be perpendicular to the top surface (Figure 14). Because of the isotropic sample properties in the planes parallel to the top/bottom surface the VOC_i flow parallel to these planes will be undetectable and will be assumed to be equal to zero. The rate (r_x) at which VOC_i will be transferred between two points (P_{X-1} and P_X) belonging to neighboring planes of isotropy is determined by the material transfer coefficient (k1) and the VOC_i concentration gradient ($C_{VOCi,X}$-$C_{VOCi,x+1}$) between the two planes. Although OSBs are not homogeneous in normal (vertical) direction, for simplicity it will be assumed that they are. As a result, the VOC$_i$ material transfer coefficient will be the same for the whole path P0-P10 in Figure 14.

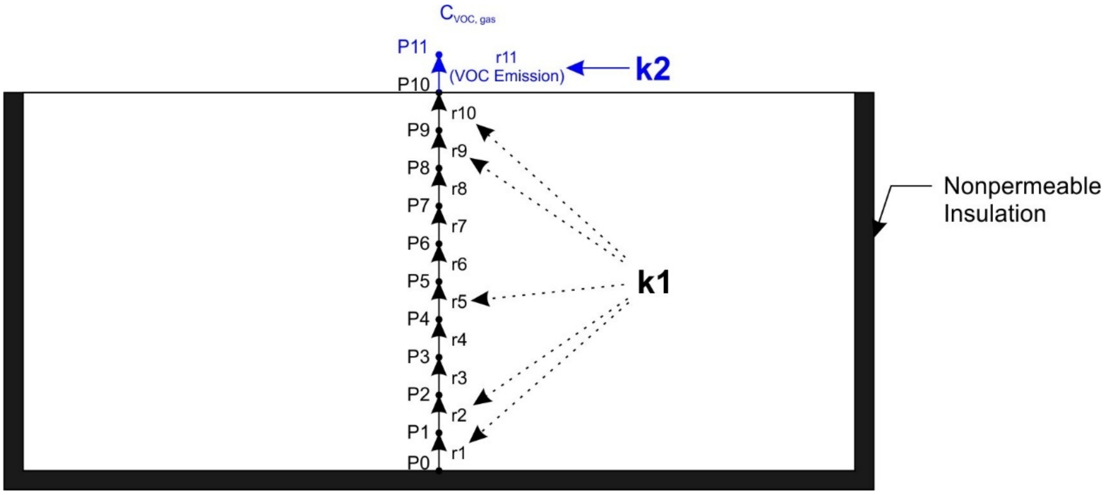


Figure 14. Vertical VOC$_i$ transfer and VOC$_i$ emission

VOC$_i$ will be emitted to the surrounding air through the exposed (top) surface at a certain rate (1).

$$r11 = k_g(k_H.C_{VOC_i,P10} - C_{VOC_i,gas}), \qquad (1)$$

where:

r11 - VOC$_i$ emission rate through point P10;
k_g - gas transfer rate coefficient;
k_H - Henry - like constant, specific for the combination of VOC$_i$ and sample material;
$C_{VOCi,P10}$ - VOC$_i$ concentration in the top layer;
$C_{VOCi,gas}$ - VOC$_i$ concentration at P11.

Because the constants k_g and k_H are difficult to be practically determined for each exposition scenario a simplification of (1) should be considered. The simplification bases on the fact that the multiplication $k_H.C_{VOCi}$ is expected to be from three to four orders of magnitude larger than $C_{VOCi,gas}$ which for alpha-pinene (typical primary pinewood VOC) is in the range 300-3000 µg/m³ :

$$k_H.C_{VOC_i,P10} \gg C_{VOC_i,gas} =>$$
$$r11 \approx k_g.k_H.C_{VOC_i,P10} =>$$

$$\boldsymbol{r11 = k_2 C_{VOC_i,P10}} \quad \textbf{(2)}$$

K2 will be called VOC$_i$ emission coefficient which is only dependable on the VOC$_i$ concentration in the surface layer of the sample.

In order to simulate the VOC$_i$ transport along the P0-P11 path and especially the VOC$_i$ emissions (r11), a 50-points model was constructed by using the Vensim® simulation software (Ventana Systems). The numbering of the variable points in the model follows the scheme P000, P002, P004, …, P100. Because this model represents a 5-fold increase in the resolution of the discrete path (P0-P10) on Figure 14, each point from the range P0-P10 on Figure 14 has its spatial equivalent in the model. For example, P000 in the model is equivalent to P0 on Figure 14, P050 to P5 and P100 to P10. Each point in the range P000-P100 is defined as a level variable in the software with initial value C0. Each two adjacent points are connected with a rate tool and this rate is defined with the following equation:

$$r_x = k_1(P_{x-1} - P_{X+1}) \qquad (3)$$

The VOC$_i$ emission rate (r11) on Figure 14 is represented in the model by a sink (cloud) rate function exiting from P100 and named "emission top". The "emission top" rate is defined with the following equation:

$$emission\ top = k_2 P_{100} \qquad (4)$$

The hypothetical emission from the bottom of the sample is also provided through the cloud rate function "emission bot" exiting from P000 and defined with the equation:

$$emission\ bot = k_2 . permeability . P_{000} \qquad (5)$$

In analogy to "emission top" the surface layer concentration (P000) and the emission coefficient ($k_{2,bot}$=$k_{2,top}$=k_2) play an important role for predicting the VOC$_i$ flow. The "permeability" variable (taking values from 0 to 1) denotes to what extend P000 is permeable for VOC$_i$ emissions. It was introduced to the model in order to enhance its flexibility in simulating emissions not only from the top but also from the "bottom" sample's surface. By taking values in the range 0 ≤ "permeability" ≥ 1, this variable could also be used for the simulation of insulation layers (like aluminium duct tape for example).

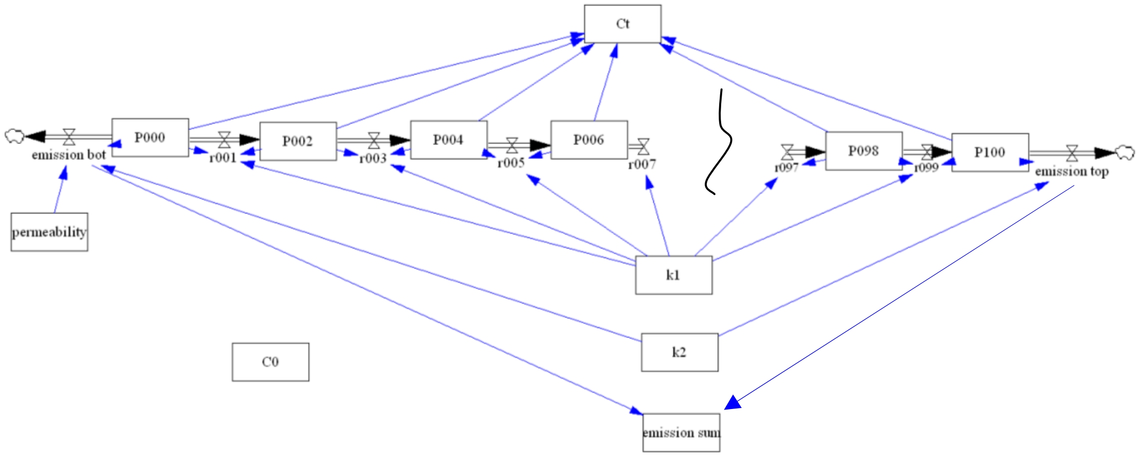


Figure 15. Simulation of linear VOCi flow path with Vensim® - model "Build Window

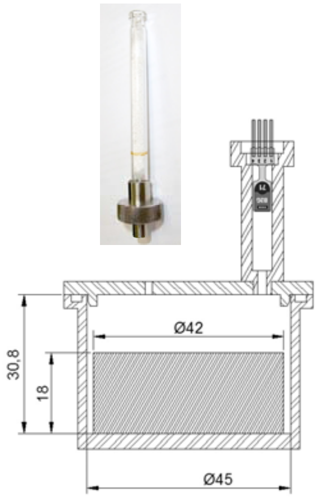
"Emission top" and "emission bot" are summed up in the variable (of type auxiliary) "emission sum", which represents the total VOC_i emission.

$$\text{emission sum}=f(t)=C_{\text{alpha-pinene},t} \quad (6)$$

The (auxiliary) variable C_t represents the average VOC_i concentration (Equation 7).

$$C_t = average(P001{:}P100) \quad (7)$$

In order to feed the model with realistic data the alpha-pinene (primary VOC) emissions from a real micro-chamber (Markes® µCTE120) measurements were taken as source (Figure 16).



Experiment name	OSB08
Sample type	OSB
n	10
Sample height [mm]	18
Aluminium foil tape	not used
Experiment duration [days]	28
Sample diameter [mm]	42
Average temperature [°C]	24,4±0,4
Average relative humidity [%]	49±2
Exposed sample area [m^2]	1,39E-03
Air flow rate [ml/min]	23,9
Air exchange rate [h^{-1}]	73,1
Loading factor [m^2/m^3]	70,7
Area specific air exchange rate - q [$m^3.m^{-2}.h^{-1}$]	1,0

Figure 16. Experiment for feeding the Vensim model with real data.

Here it should be explicitly pointed out that the usual test chamber measurements deliver concentration-values [µg/m³] and not emission-values [µg/h] as results.

However, under the assumptions pointed in paragraph (9.3.4) VOC concentrations measured in micro-chambers correlate very well with VOC emission rates. Therefore in order to explore the behavior of the model and the dependencies between the different parameters (but not the absolute emissions or concentrations), the values of the variables were set so, that the model delivered "emission sum values" almost identical to the real alpha-pinene concentrations, which had been measured in the micro chamber (Figure 17).

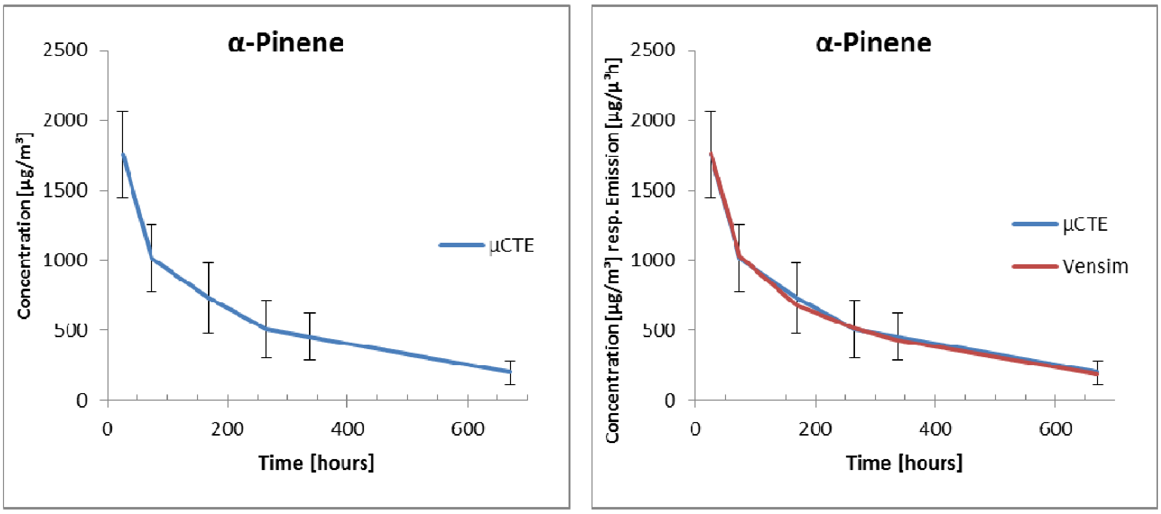


Figure 17. Comparison of the alpha-pinene concentrations measured during real experiment (OSB08) in µCTE microchambers (n=10) and the Vensim®-modelled VOC$_i$ emissions

In order to obtain the model solution on Figure 17 (right) the input variables had to take the following empirically derived values: P000 = P002 = … = P100 = C0 = 9700 µg; k1 = 2.6 µg/h; k2 = 15 µg/h; permeability = 0. The "Time Boundaries" settings of the model were set as follows: INITIAL TIME = 0; FINAL TIME = 672; TIME STEP = 0.0078125; SAVEPER = 1; Units for Time = Hour; Integration Type = Euler.

It has to be stated that the values of C0, k1, k2 and "permeability" were not expected to be equal to any real corresponding concentration or coefficient in the micro chamber experiment. However since they lead to realistic behavior of the model "emission sum"=f(t), the proportions between them should be realistic. The realistic proportions could be used for drawing conclusions about the VOC$_i$ transport inside the test specimen and respectively the VOC$_i$ emissions. Thus, based on the k1 and k2 values, as well as on equations (3) and (4) it could be stated that the VOC$_i$ transfer at the top boundary layer (P100→air) has the potential to take place at much higher rate than the transfer inside the sample volume. It is the transfer inside the sample volume which is the limiting factor for the VOC$_i$ transport. This could be confirmed by changing the k2 value in Vensim® and examining its influence on the emissions. It could be confirmed (not shown) that even setting k2 to values higher than 15 without changing k1 has almost no effect on the emissions. Unfortunately, because of technical limitations the maximal boundary transfer rate could hardly be measured and thus the experimental determination of k2 is not very possible.

There is however at least one important erroneous assumption in the statements above which deserves to be corrected and further investigated. The permeability of the "bottom" layer was set to zero but since the edges of the samples in the real experiment were not sealed it is clear that the top surface (declared as exposed surface) is not the only surface which emits VOC. Since the model proposed in Figure 15 is one dimensional and cannot simulate emissions from the edges of the test sample the only position which could also be set to emit VOC was the bottom surface.

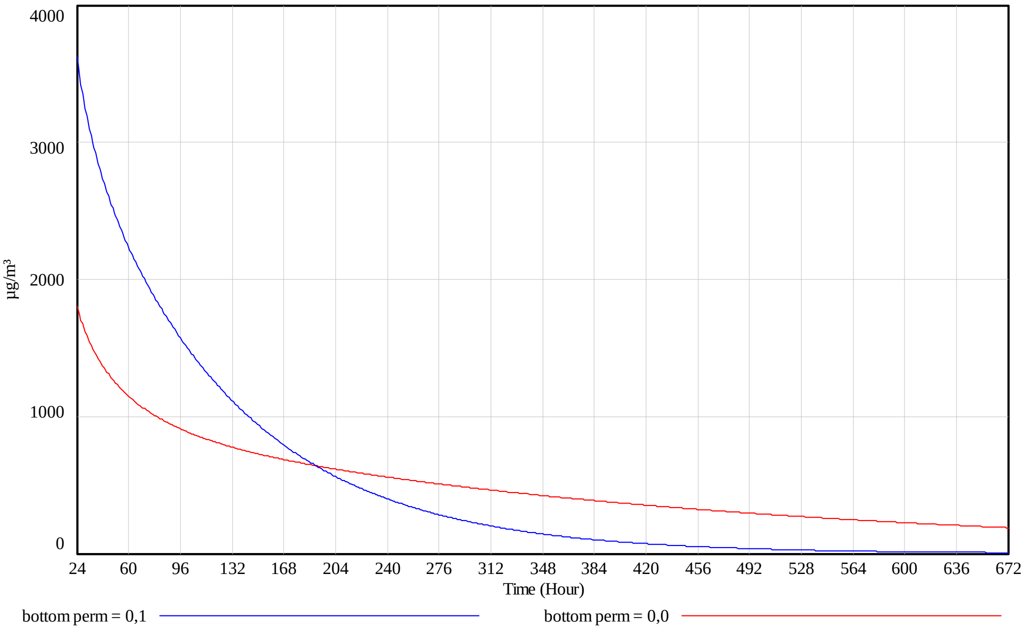


Figure 18. Vensim simulation of alpha-pinene emissions from samples with different permeability of their bottom layers

The comparison on Figure 18 indicates that unconsidered surfaces with low permeability (0.1) have strong impact on the VOC emission model defined above.

Figure 19 shows the results for an adapted model for which the permeability of the bottom layer was left 0.1 but other parameters (k1) were changed in order the model to derive results as close as possible to the real experiment data (shown at Figure 17 left).

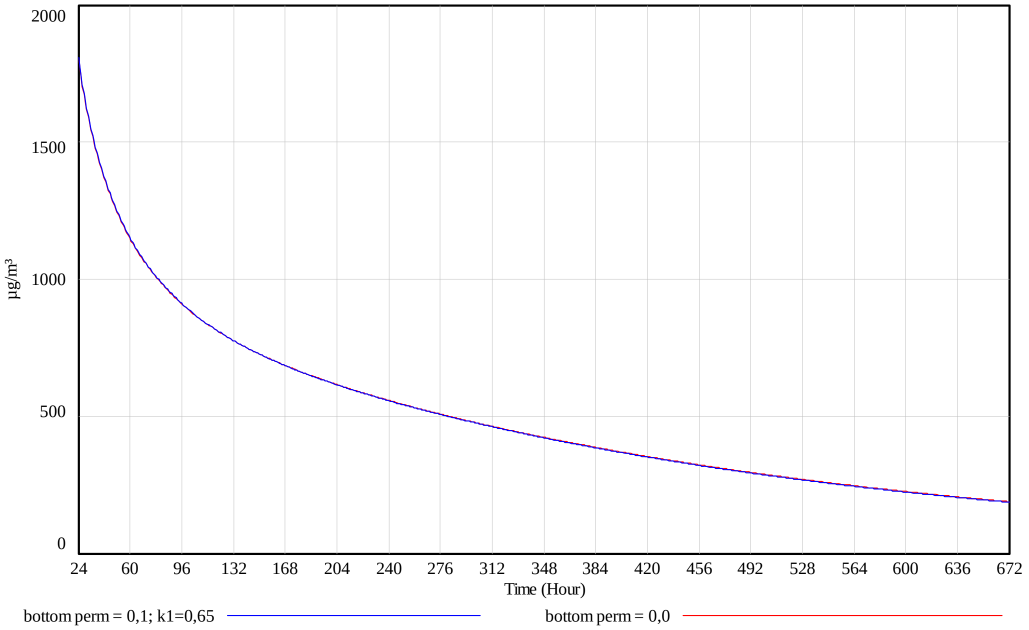


Figure 19. Results from an adapted model with permeable bottom surface (blue) compared to the model with impermeable bottom surface introduced in Figure 17 right (red)

The following values were derived: P000 = P002 = … = P100 = C0 = 9700 µg; k1 = 0.65 µg/h; k2 = 15 µg/h; permeability = 0.1; INITIAL TIME = 0; FINAL TIME = 672; TIME STEP = 0.0078125; SAVEPER = 1; Time units = Hour; Integration Type = Euler.

Important characteristic of the model with these settings is that it is much more stable to further changes in the permeability of the bottom layer (Figure 20).

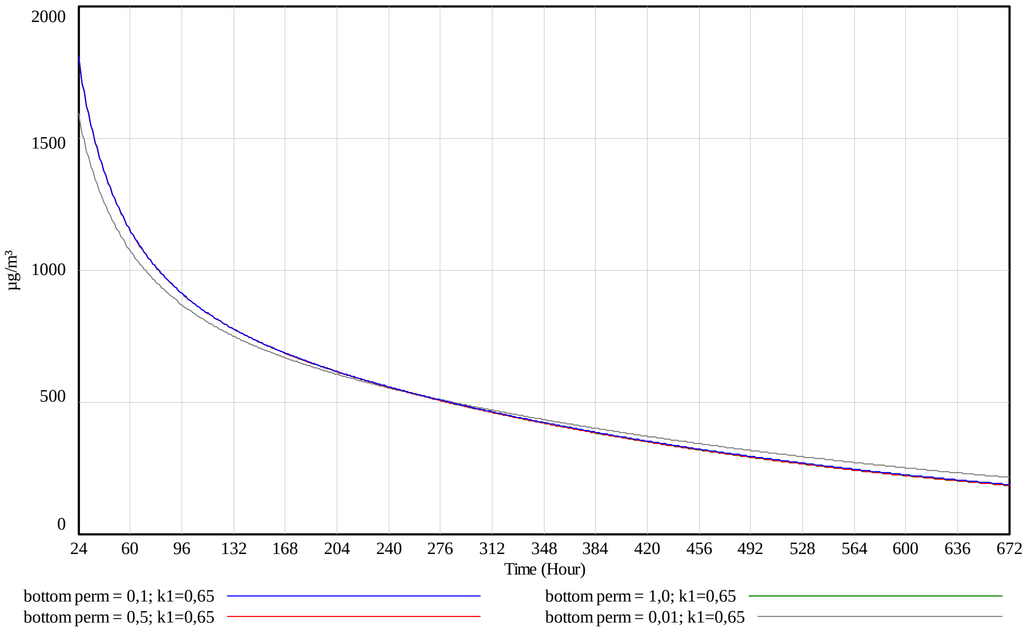


Figure 20. Influence of the bottom permeability on the summary VOC_i emissions

9.3.2. VOC emissions from unsealed edges

The structure of many wood based products is anisotropic. OSB for example is built up from cross-oriented layers of thin, rectangular wooden strips. This oriented anisotropy implies that the transport of fluids in the different directions would have different mechanism. Figure 21 illustrates the characteristic transport directions inside an OSB plate, which are solely determined by the specific arrangement of the wooden stands.

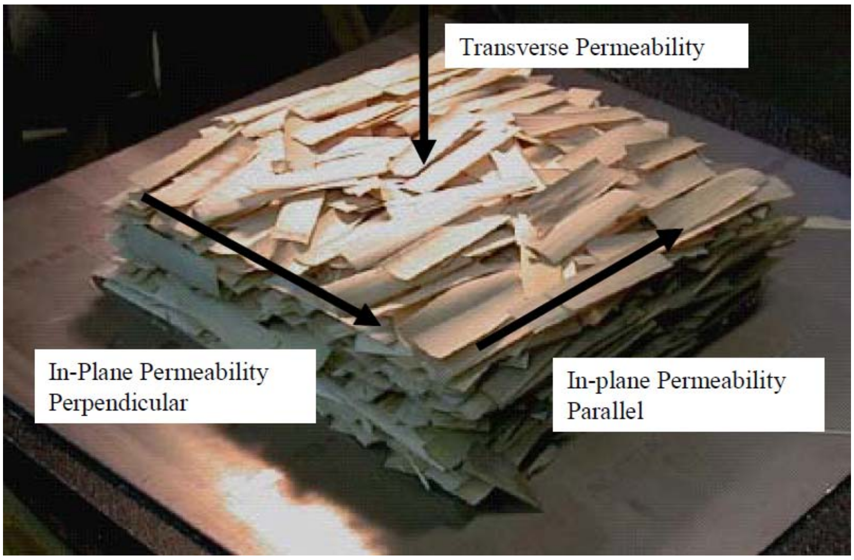


Figure 21. Characteristic VOC permeability directions inside OSB (Hood 2004)

In this case, because of the specific orientation of the macroscopic structures, the VOC conductivity in the pointed directions could be expected to be different. It was reported that the In-plane permeability for OSB is about ten times higher than the transverse permeability for boards with density of 600-800 kg/m³ (v. Haas, G. et al. 1998).

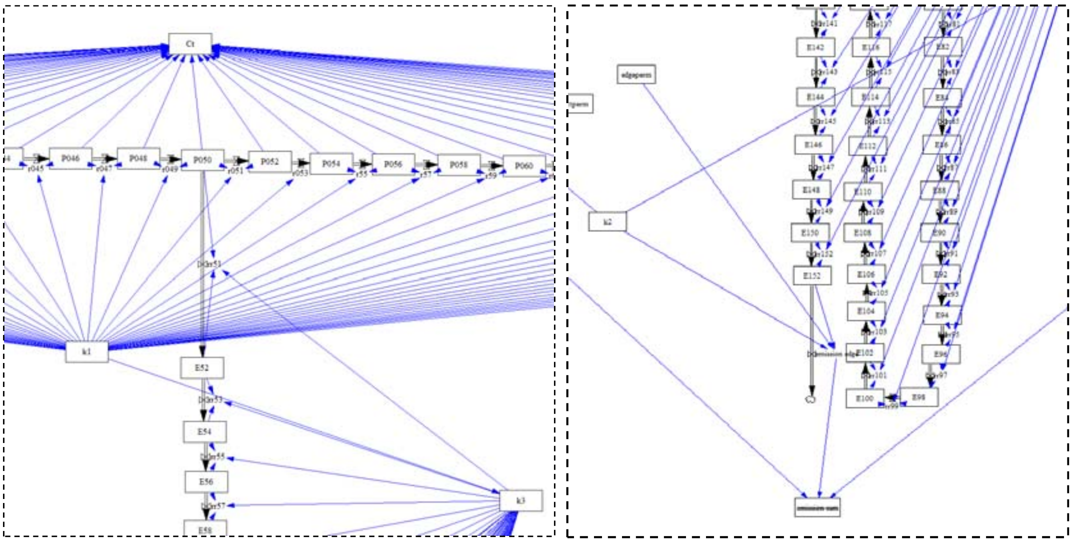


Figure 22. Introducing of edge emitting surface in the Vensim model

In order to examine the influence of the edge surface on the VOC emissions an "edge VOC pathway" was introduced starting from the middle element of the existing Vensim model (Figure 21). It consisted of 51 additional elements of type "level" connected with "auxiliary" rates (fluxes) defined as follows:

$$rr_x = k_3(E_{x-1} - E_{X+1}) \quad (8)$$

In accordance with the literature information (v. Haas, G. et al. 1998) k3 was set to be equal to: $k_3 = 10k_1$. The total VOC_i capacity of the virtual sample was preserved by reducing the individual point concentration C0 to 4850 µg/point. The boundary layer VOC transport was defined in the same way as the top and the bottom surface:

$$emission\ edge = k_2 E_{152} \quad (4)$$

Thus, the influence of the "edge" could be visualized on Figure 23.

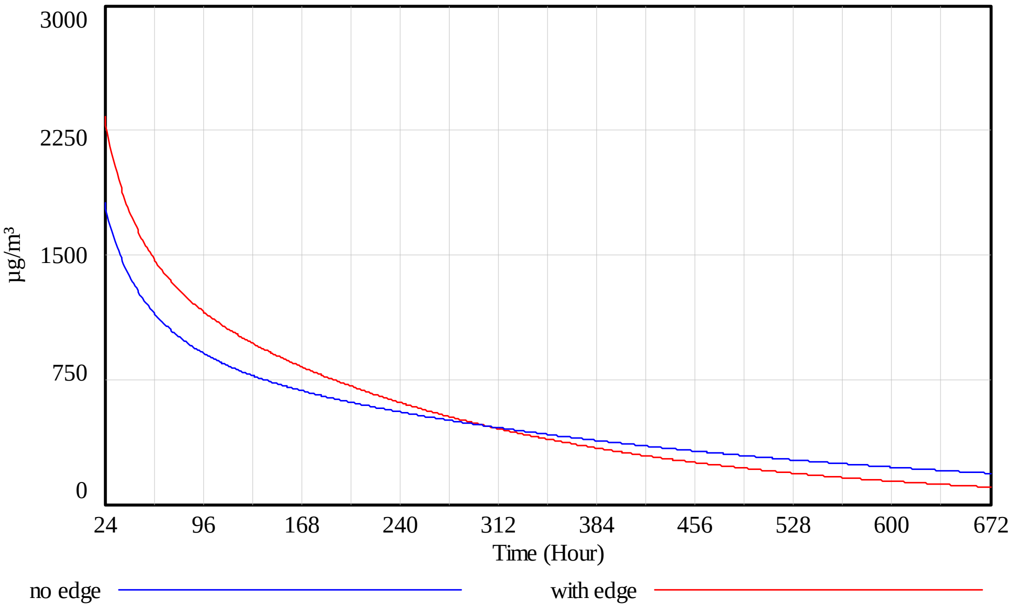


Figure 23. Influence of an unsealed edge with surface equal to the top surface to the VOC emissions

The pattern of Figure 23 resembles to this of the experimental results presented on Figure 41 however there are some sensible considerations which should be made when driving conclusions about the results presented on Figure 41 like for example the unusual high proportion of edge- to normal emitting surface, the introduction of highly VOC-loaded surfaces to the measurement system through cutting and the reduction of the length of the "edge" pathway (9.3.3) or the different emissions formation of primary and secondary VOC and the permeability of the sealing tape (9.1 and 9.4.4). Unfortunately, these considerations could not be implemented in the current model since they suppose the creation of at least 2D finite elements model.

Finally, the "edged" model was adapted in order to yield results as close as possible to the experimental data (Figure 24). The following values were derived: P000 = P002 = … = P100 = E52 = … = E152 = C0 = 4850 µg; k1 = 0.4 µg/h; k2 = 15 µg/h; bottperm = 0.1; edgeperm = 1; INITIAL TIME = 0; FINAL TIME = 672; TIME STEP = 0.0078125; SAVEPER = 1; Time units = Hour; Integration Type = Euler.

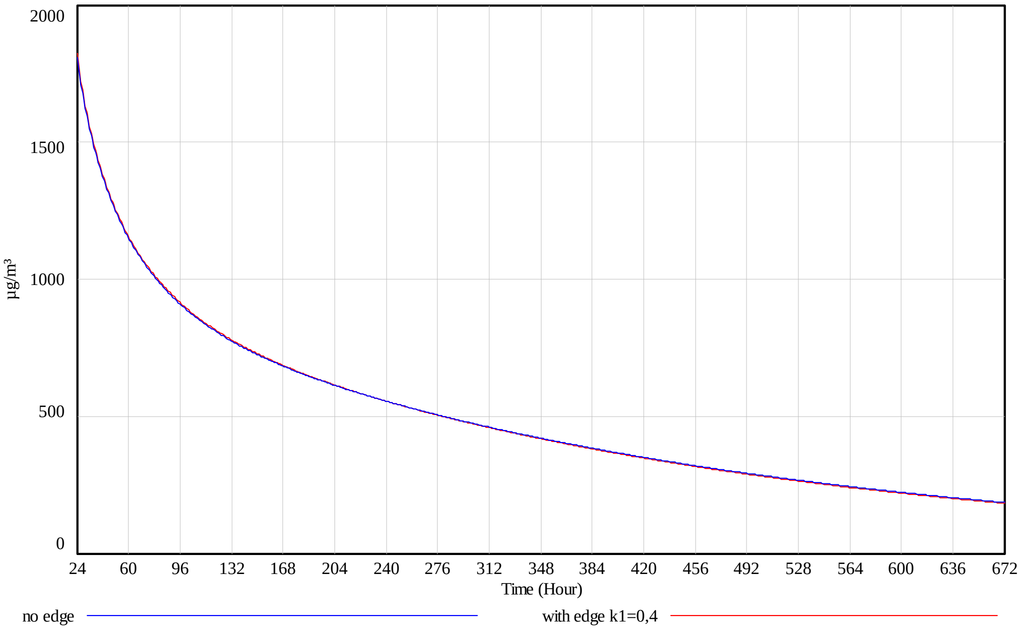


Figure 24. Results from an adapted model with an "edge surface" compared to the previous model without "edge surface"

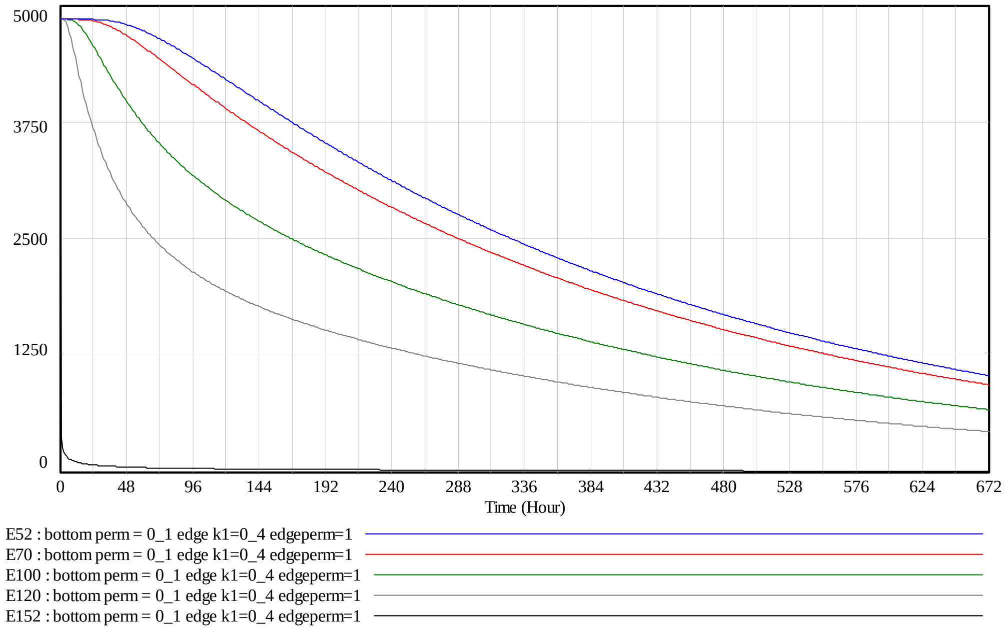


Figure 25. Distribution of the VOC concentrations along the edge pathway by 28 days simulation

9.3.3. Scaling down VOC measurement setup

There are several considerations which should be made when scaling down test specimens for the purpose of VOC emissions evaluation:

- The change in the proportion of the face emitting area to the edge emitting area. The scale of the change correlates with the factor of reducing the original size of the product to be tested;
- The change in the proportion of the “normal” VOC pathway length to the “edge” VOC pathway length E_0/N_0 (8). This change could have impact in cases where the transverse and the in-plane permeability differ like for example OSB.

$$\frac{E_O}{N_O} \neq \frac{E_{SS}}{N_{SS}} \quad (N_O = N_{SS}) \qquad (8)$$

- Due to the cutting, VOC saturated layers from the test specimen’s core are exposed as outside layers of the small-scaled sample (Figure 25). This could lead to dissimilarities in systems where specimen edges are not sealed.

All three factors lead to deviations from the original proportions of the transfer fluxes which causes dissimilarity in the two systems described with the following inequality:

$$\frac{\sum To}{(\sum IPo+\sum IP'o)} \neq \frac{\sum Tss}{(\sum IPss+\sum IP'ss)} \qquad (9)$$

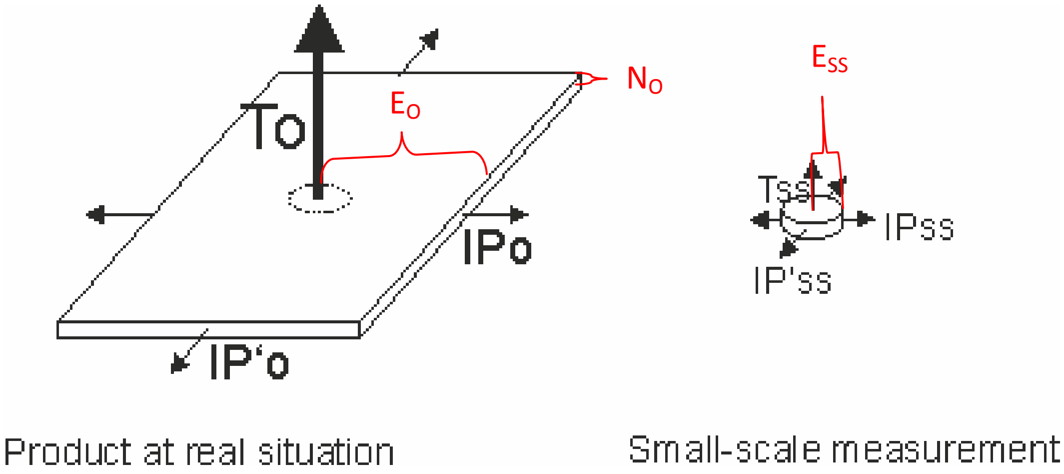


Figure 26. Reduction of the in-plane VOC-path as a result of scaling down of the sample

Where:

To - Original transverse VOC flux
IPo - Original in-plane VOC flux (parallel)
IP’o - Original in-plane VOC Flux (perpendicular)
E_O - Original edge VOC pathway (similar to the model description Figure 22)
N_O - Original normal VOC pathway ($N_O = N_{SS}$)

Tss	- Small-Scale transverse VOC flux
IPss	- Small-Scale in-plane VOC flux (parallel)
IP’ss	- Small-Scale in-plane VOC flux (perpendicular)
E_{SS}	- Small-Scale edge pathway

In order to correct the (most obvious) first distortion the edges of the small-scale test specimens are usually sealed to that extend at which the face emitting area to edge emitting area proportion is preserved. It is obvious that this approach does not correct the second and the third dissimilarities.

Another fact that is normally being neglected (also in this work - 9.3.2) is that the structure of softwood engineered panels predetermines the existence of at least tree VOC transport mechanisms for wood products with intact wood fibers. For example, in the case of OSB at one side there are the cavities at random positions and with random dimensions between the strands, at the other side there are the tracheids which form an oriented capillary network inside the strands and thus in the end product. The tracheids are coated with the cell walls which are characterized with another specific conductivity towards VOC when compared with the bigger cavities or the tracheids’ voids. A simplified 2D lattice which resembles the possibility for building up Lattice-Boltzmann models with multi-mechanism VOC-transport is proposed on Figure 27. Such models should be much more resistant to “scale-down” errors and should be able to predict more precisely real indoor concentrations when the results of small-scaled chamber measurements are being used as base for these predictions.

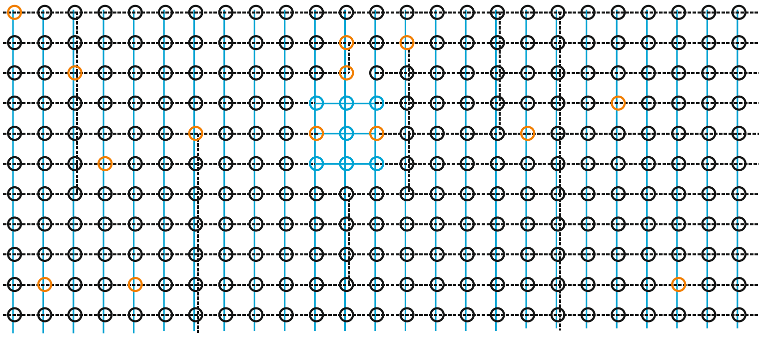


Figure 27. 2D lattice for describing multi-mechanism model for VOC transport inside the sample: Blue lines gaseous diffusion (mainly through the cell walls); Dotted lines capillary transport (transport inside the traheids); Black nodes – predominating junctions; Blue nodes – cavities; Brown nodes – capillary openings.

Another observed problem is that the widely-used edge-sealing aluminum foil (3M) is to some extend permeable for VOC (9.4.3).

9.3.4. Convertions from VOC concentrations to VOC emission rates

If a freshly produced softwood sample in a test chamber is being tested (Figure 28 left) it could be stated that both the sample and the chamber are sources of VOC emissions: VOC_{Es}, VOC_{Etc}. In the early stages of the experiment after the sample has been introduced into the chamber there should be a difference between both emission rates ($VOC_{Es} > VOC_{Etc}$) because it takes time until the chamber is uniformly filled with the emitted substances. After certain initial time period (**$t_{initial}$**) the VOC emissions from the chamber should start to be equal to the VOC emissions from the sample ($VOC_{Es} = VOC_{Etc}$). The assumption that the last hypothesis is false would mean that:

- $VOC_{Es} > VOC_{Etc}$ – a constant accumulation of VOC in the chamber will take place or
- $VOC_{Es} < VOC_{Etc}$ – the VOC concentration inside the chamber at some time will be lower than zero.

Knowledge about $t_{initial}$ is important because all IAQ-assessment measurements are supposed to be done after this time period has been elapsed. This will guarantee that the measured VOC concentrations in the chamber can be converted in VOC chamber emissions and these emissions would correspond to the sample VOC emissions (ECA-IAQ 1997a) .

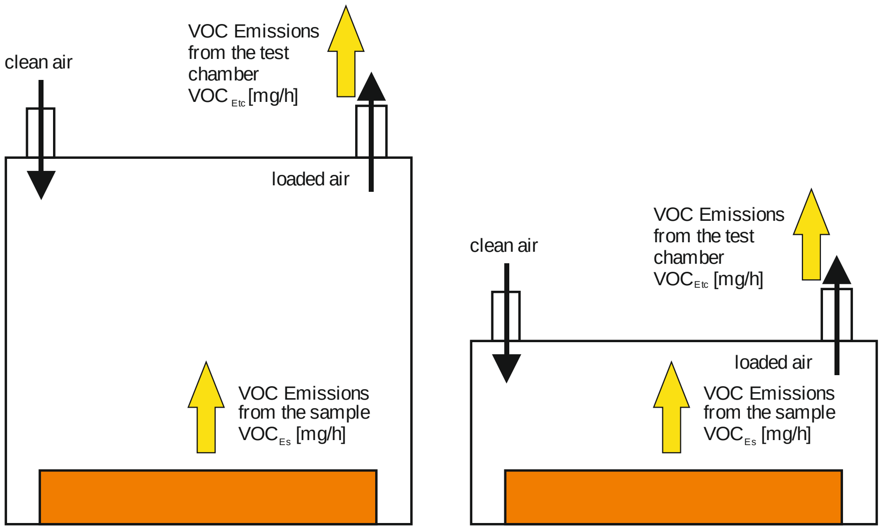


Figure 28. Setup for testing VOC emissions at different loading factors and air exchange rates

If the same experiment is conducted under identical conditions (like temperature, humidity, air mass flow, material type and size of the test specimen) but in a smaller chamber (Figure 28 right) the air change rate will be increased proportional to the volume reduction. It is of interest what impact would this increase have on $t_{initial}$.

In order to simplify the answer of this question it will be assumed that the impact of the air change rate on the sample VOC emissions can be neglected. It will be also assumed that the chamber walls have sink effect on the chamber VOC concentrations (but no effect on the sample VOC emissions) and the maximal capacity of this "sink" was chosen to be 0.35% from the total VOC amount (potential) in the sample. The Vensim model displayed on Figure 29 was built in order the solution of the problem to be visualized.

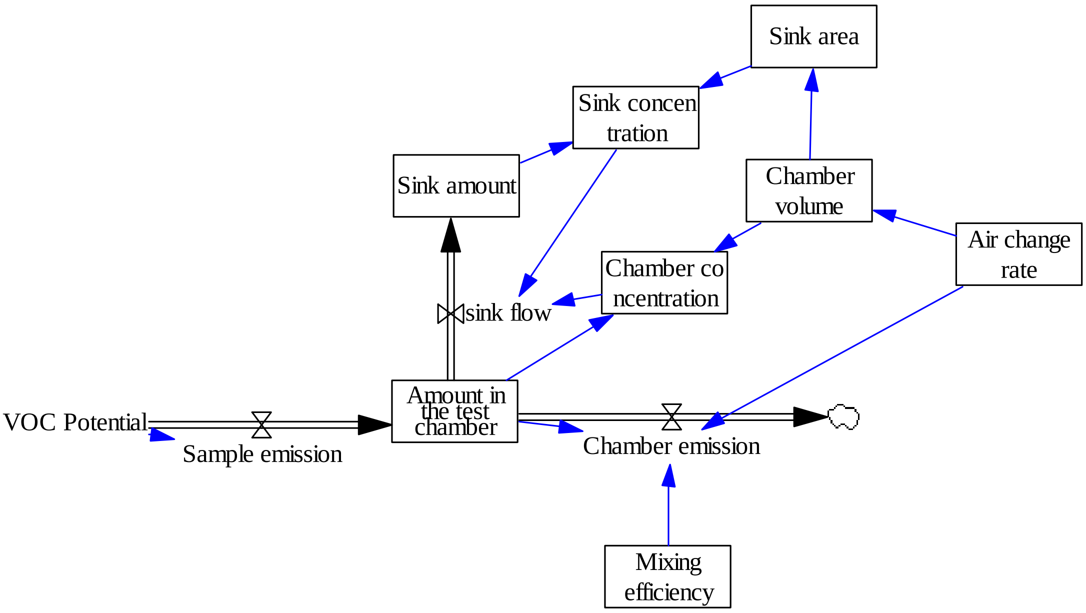


Figure 29. Scheme of the Vensim model for simulating emissions at different air change rates

Initial time=0; Final time 672; Time step 0.0078125; SAVEPER 0.1; Units for time hour; Integration type Euler; Program version 6.2 (x32)
VOC Potential: Level (Initial value **10000** mg);
VOC Potential = - Sample emission;
Amount in the test chamber: Level (Initial value 0 mg);
Amount in the test chamber = Sample emission-sink flow-Chamber emission;
Mixing efficiency: Constant = 0.95;
Air change rates: Constant=0.25, 0.5, 1, 1.5, 50;
Chamber volume: Auxiliary = 1/Air change rate;
Sink area: Auxiliary = Chamber volume^(2/3);
Chamber concentration: Auxiliary = Amount in the test chamber/Chamber volume;
Sink concentration: Auxiliary = Sink amount/Sink area;
Sink flow: Auxiliary = (Chamber concentration-Sink concentration***3**)***0.05**;
Sink amount: Level (Initial value 0 mg);
Sink amount = sink flow;
Sample emission = **0.005***VOC Potential;
Chamber emission = Amount in the test chamber*Air change rate*Mixing efficiency;

The variables marked in blue were chosen so that the sample emissions decay curve on Figure 30 to have similar shape to the curves derived from real observed data (reference).

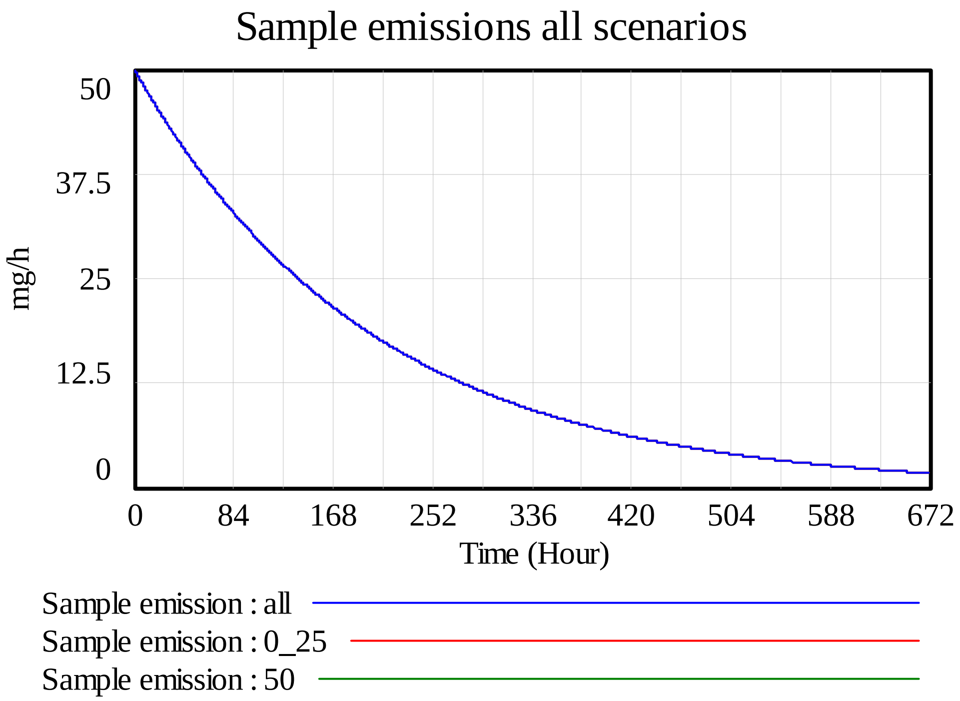


Figure 30. Sample emissions decay curve of the model

Five scenarios with five different air change rates were simulated (Table 5) and it can be seen that the sample emissions curves in all scenarios are identical (Figure 30). This could not be said for the initial times (Figure 31 and Table 5). It could be stated that higher air exchange rates are critical if the purpose of the analytics is to characterize the sample emissions rapidly. In such cases measurements according ISO 16000-25 (µCTE) or modified ISO 16000-10 with a FLEC cell used as a lid of a cylindrical chamber would be beneficial. However, especially in the case of the microchambers, pronounced scaling down and edge effect interferences should be taken into account (9.3.3 and 9.4.4).

Table 5. Initial times for measurements at different air change rates

Air change rate [1/h]	Volume [m³]	Testing method	$t_{initial}$ [h]
0.25	4.0	CEN/TS 16516$_{min}$	~21
0.5	2.0	AgBB	~15
1.0	1.0	EN 717-1	~12
1.5	0.67	CEN/TS 16516$_{max}$	~9
>50	0.02	µCTE (ISO 16000-25) FLEC (ISO 16000-10)	<2

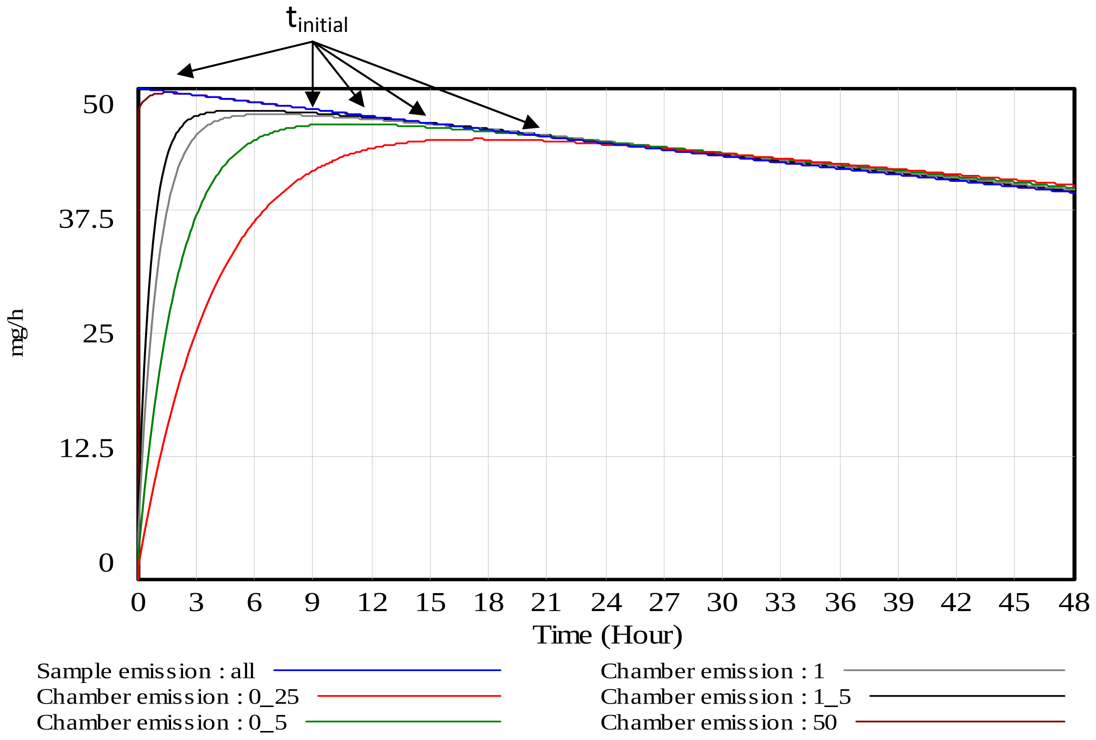


Figure 31. Chamber VOC emissions by different air change rates

IAQ evaluation attendant analytics where the first VOC-sampling is taking place 72 hours after placing the sample will not be affected from problems with the conversion of concentrations into emissions unless the air change rate is very low (<0.08).

9.4. µCTE – a convenient tool for rapid research and in-factory production monitoring

9.4.1. Estimating the air velocity above test specimen's surface

One of the challenges when using µCTE as a testing chamber for VOC* emission measurements is the determination of the air velocity above the test-specimen's surface. Such determination is necessary because the majority of the procedures for IAQ assessment define certain air velocity above test-specimen's surface (usually in the range 0.1 – 0.3 m/s).

Since µCTE cell dimensions are comparatively small the usage of regular measurement techniques for determining air velocity would have biased the real velocity value. In 2007 Schripp et al. used computational fluid dynamics method (CFD) to estimate the velocity profile over the bottom of an empty µCTE cell (Schripp et al. 2007). In early 2008 Markes changed the position and reduced the diameter of the cell's inlet and outlet (Figure 32) and therefore it was expected that the air velocity profile could also have been changed. In the course of this dissertation the author made a CFD simulation in a µCTE mesh with the updated dimensions by using Gambit® (for building the mesh) and Fluent® (for the simulation). A visual comparison between the new air velocity profile and the old one is depicted on Figure 33.

It could be stated that the velocity pattern did not change much as result of the changes in the dimensions and the position of the inlet/outlet. The flow remained laminar with two characteristic vortexes at both sides of the inlet. However, because of the decrease of the inlet/outlet diameter, an increase of the velocity was observed. The flow with increased air velocity (>0.03 m/s) covers brighter area above the bottom of the cell and is more symmetrically distributed.

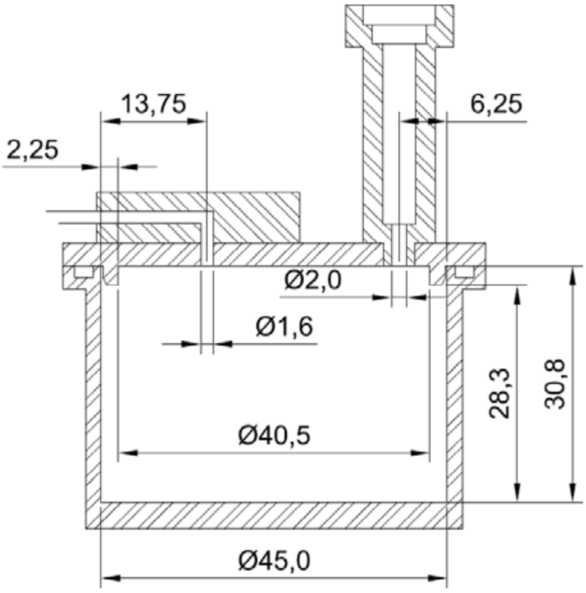


Figure 32. CFD simulation relevant dimensions of the current (model 2009-2012) Markes® micro chambers

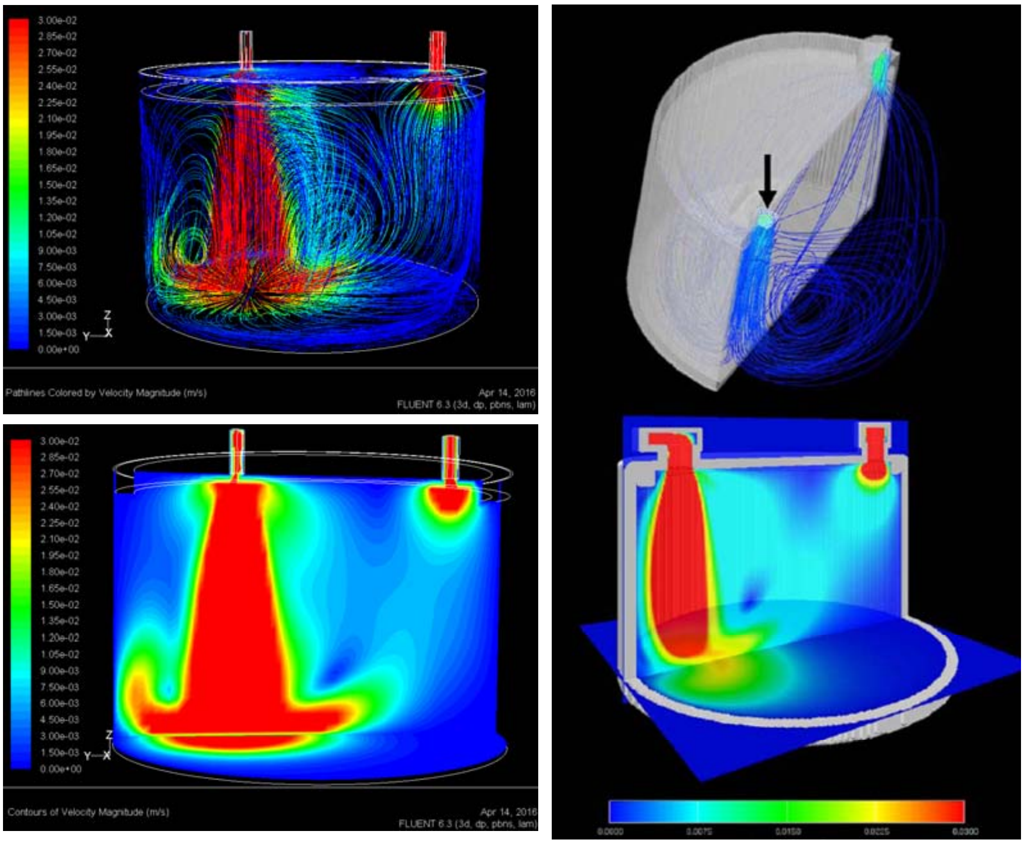


Figure 33. Comparison between the velocity profiles in µCTE chambers with different positions and dimensions of their inlets and outlets as well as different airflows. Left: Markes model after 2008 with app. 80 ml/min air flow (Stratev); Right: Markes model prior 2008 with 100 ml/min air flow (Schripp et al. 2007).

By using the same CFD simulation methods as the described above the author was able to calculate air velocities in chambers loaded with samples and to draw conclusions about the influence of the air velocity on VOC emissions from pinewood products (9.4.2).

9.4.2. VOC emissions evaluation: Influence of air velocity on VOC emissions from engineered pinewood panels (OSB)

Air velocity above test specimen's surface is a parameter which (according all European VOC-emissions evaluation standards) is important and should be controlled and monitored. Normally for solid (or liquid)/gas boundary interfaces the increase in air velocity leads to an increase in the evaporative mass transfer. If air velocity in a VOC emissions testing chamber is increased this should lead to an increase in VOC emissions. Practically this occurrence could be hardly observed in cases where the limiting factor for the evaporative mass transfer is the diffusion rate inside the test specimen. If internal diffusion rate is too low in comparison to the velocity of crossing the boundary layer, then the increase of air velocity would not contribute to a significant increase of VOC-emissions.

In order this assumption to be examined for wood panels (OSB) the experiment shown on Figure 34 was conducted. Since air velocity in the microchamber's cell cannot be controlled independently (no active ventilation is present) its increase was achieved through raising the position of the test specimen (and thus decreasing the free volume) in the cell and through simultaneously increasing the flow rate. The CFD simulation (described in 9.4.1) showed that the difference (in air velocities above test specimen surfaces) between the two setups was up to three orders of magnitude: $3.10^{-6} – 3.10^{-3}$ m/s (Figure 34).

Summary if the boundary layer transition speed was relevant for altering the VOC emissions rate from OSB panels (by the conditions of the experiment) the measured concentrations in the cells with Setup 2 should be higher than the concentrations in the Setup 1 cells at Figure 34.

It should also be mentioned that the steps described above led to an increase of the air exchange rates in the cells with increased air velocity (9.3.4).

The results from the experiment are presented as the sum of the IST-corrected abundances of the characteristic ion (m/z) signals for the two characteristic chemical groups for pine wood (aldehydes and monoterpenes). This type of presentation was chosen in order to simplify quantification.

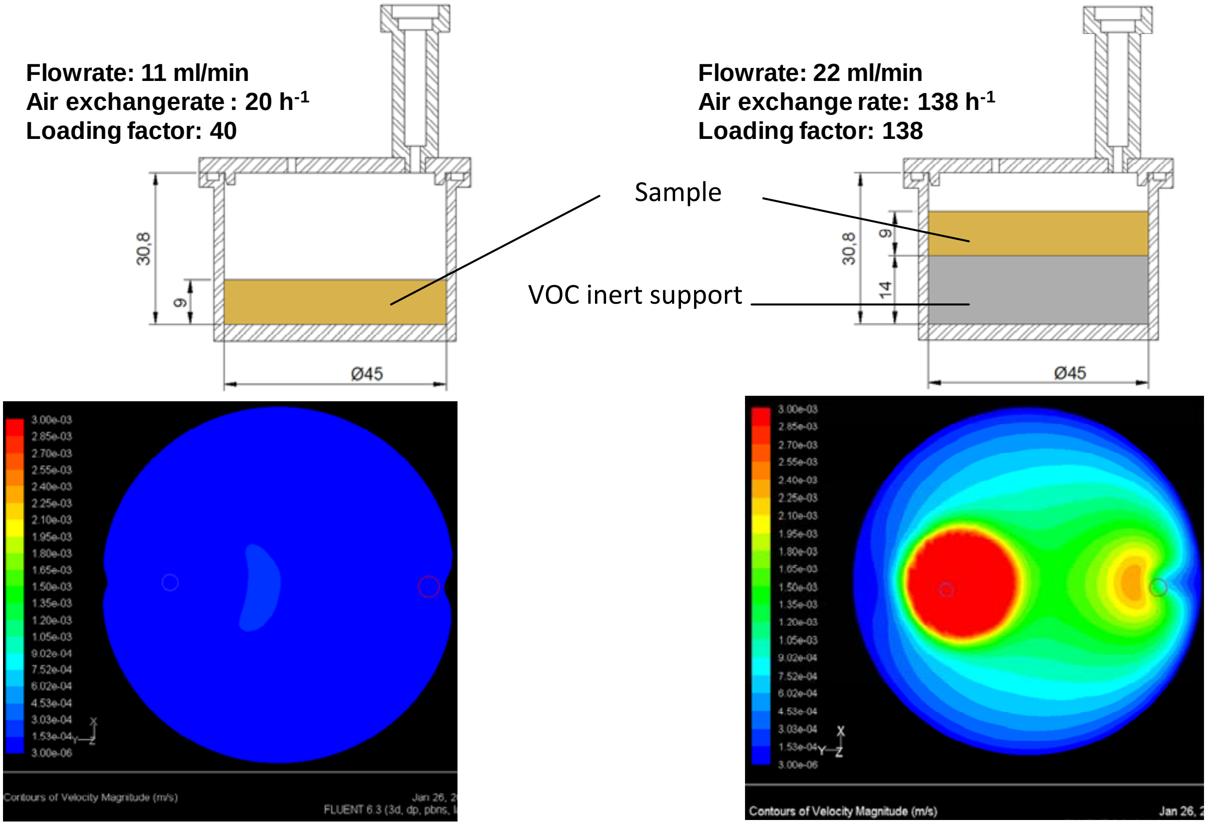


Figure 34. Experimental setup for clarifying the influence of air velocity on VOC emissions from pinewood panels (OSB). Setup 1 (left): Round test specimen (n=3) with a diameter of approx. 45 mm was put on the cell's bottom and the air flow rate was set to 11 ml/min; Setup 2 (right): Round test specimen (n=3) with a diameter of approx. 45 mm was put on a cylindrical aluminium support with height of 14 mm and the flow rate was set to 22 ml min.

Figure 35 shows that there was no significant difference in emission rates between the two setups. Analogous to the results of the mass transfer simulation in 9.3.1 the results from this experiment indicate that only the internal diffusion is relevant for VOC emission rates from OSB and not the velocity of crossing the solid/gas boundary interface.

As conclusion, it could be stated that there are indications (9.3.1 and 9.4.2) that the air velocity above test specimen's surface, the flow rate and the air exchange rates in the investigated intervals do not have significant influence on VOC emissions from pine wood based OSB. Similar conclusion was drawn from another author (Marutzky 1988) but for formaldehyde (VVOC) and particleboards. According to the source above for air velocities from 0.06 to 0.1 m/s the influence of the boundary interface on the formaldehyde emissions can be neglected. However a difference between the formaldehyde emissions determined in a ventilated chamber (with air velocity in the range 0.1-0.3 m/s) and a non-ventilated one (air velocity < 0.01 m/s) was observed. The same author has also observed that an increase of the bulk density of the particle boards leads to reduction of the emissions dependency on ventilation.

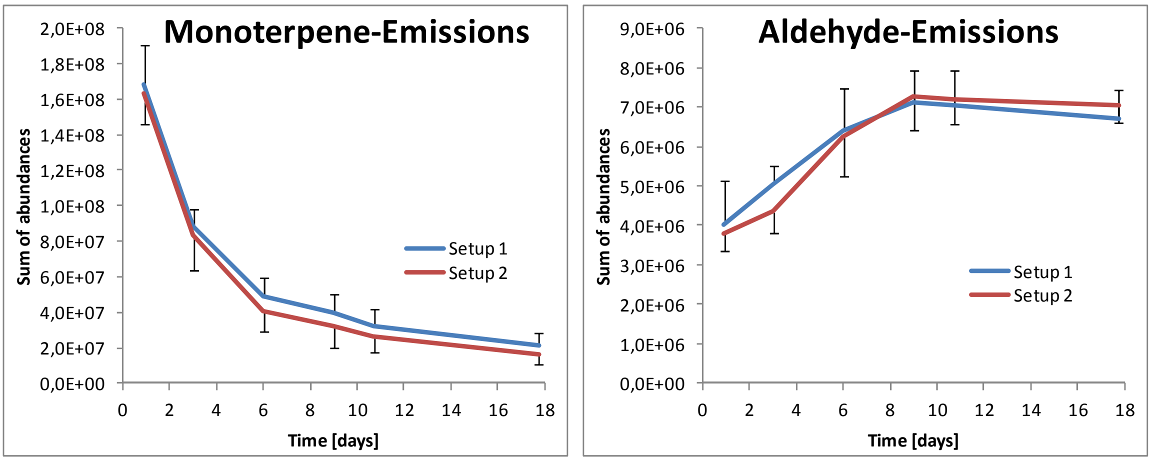


Figure 35. Results from the experiment (n=5 for each setup)

These results show that there is an open field for investigations on the influence of air velocity on the different type of emissions (primary, secondary, VOC, VVOC etc.) and from different product groups. It should also be considered that water vapor can have influence on VOC* emissions (like formaldehyde) and that air velocity can indirectly influence these emissions by intensifying water vapor exchange from the air with the sample. Not at least, it is not only the air velocity which is important but also the air flow regime above the test surface (laminar or turbulent).

9.4.3. Humidity control system

One of the limitations of the μ-CTE (in 2009) was the lack of control over humidity offered from the producer. Thus, humidity related phenomena like the formation of acetic acid (Figure 36) or formaldehyde could not be investigated properly.

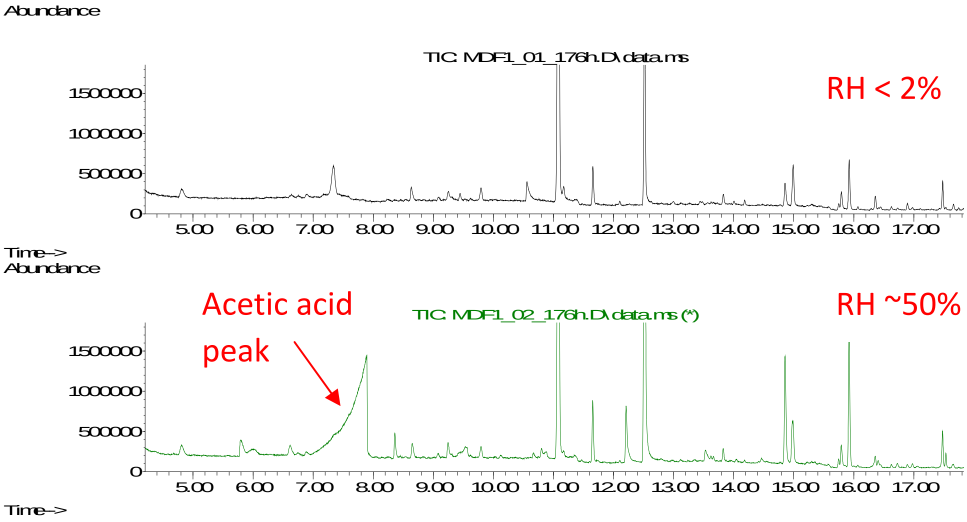


Figure 36. GC/MS Chromatograms of VOC emissions measurements from MDF tested under dry (above) and humid (below) conditions

Under the presumption that the usage of the µ-CTE for VOC*-emissions evaluation purposes would be exclusively under isothermal conditions (and the gas supply would be dried compressed air) Stratev and Srebotnik constructed a simple humidifier for the range of approximately 20% to 85 %RH based on one Peltier element (Figure 37). Major advantages of this construction were that it was inexpensive, reliable, and did not produce aerosol droplets. Further development of the humidifier which was enrolled as a registered design in Austria led to implementing the possibility to independently set the humidity in each cell of the µ-CTE (Stratev, Srebotnik 2011) (Figure 38 and Figure 39).

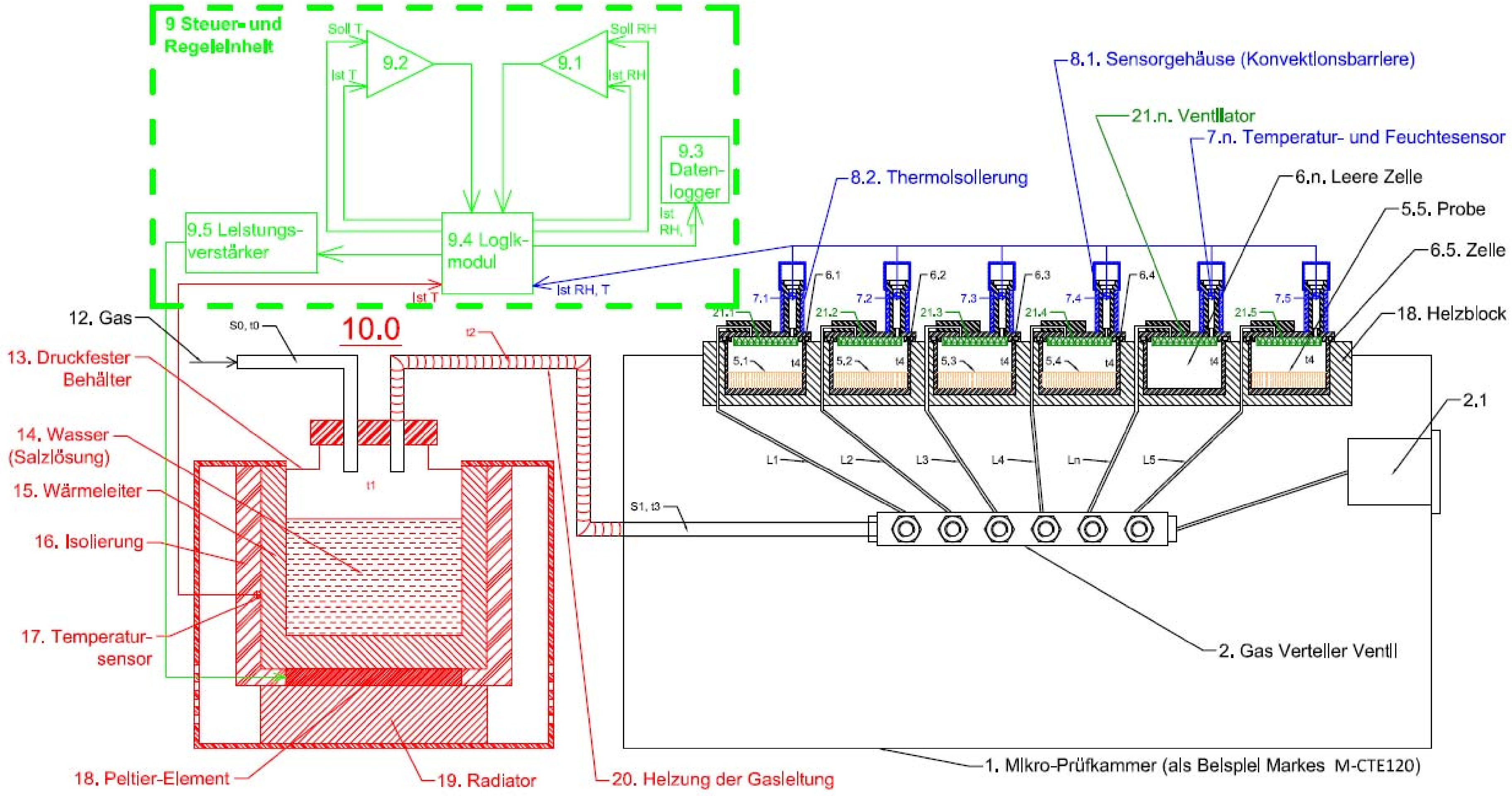


Figure 37. Humidity control system (Stratev and Srebotnik) for micro-chamber

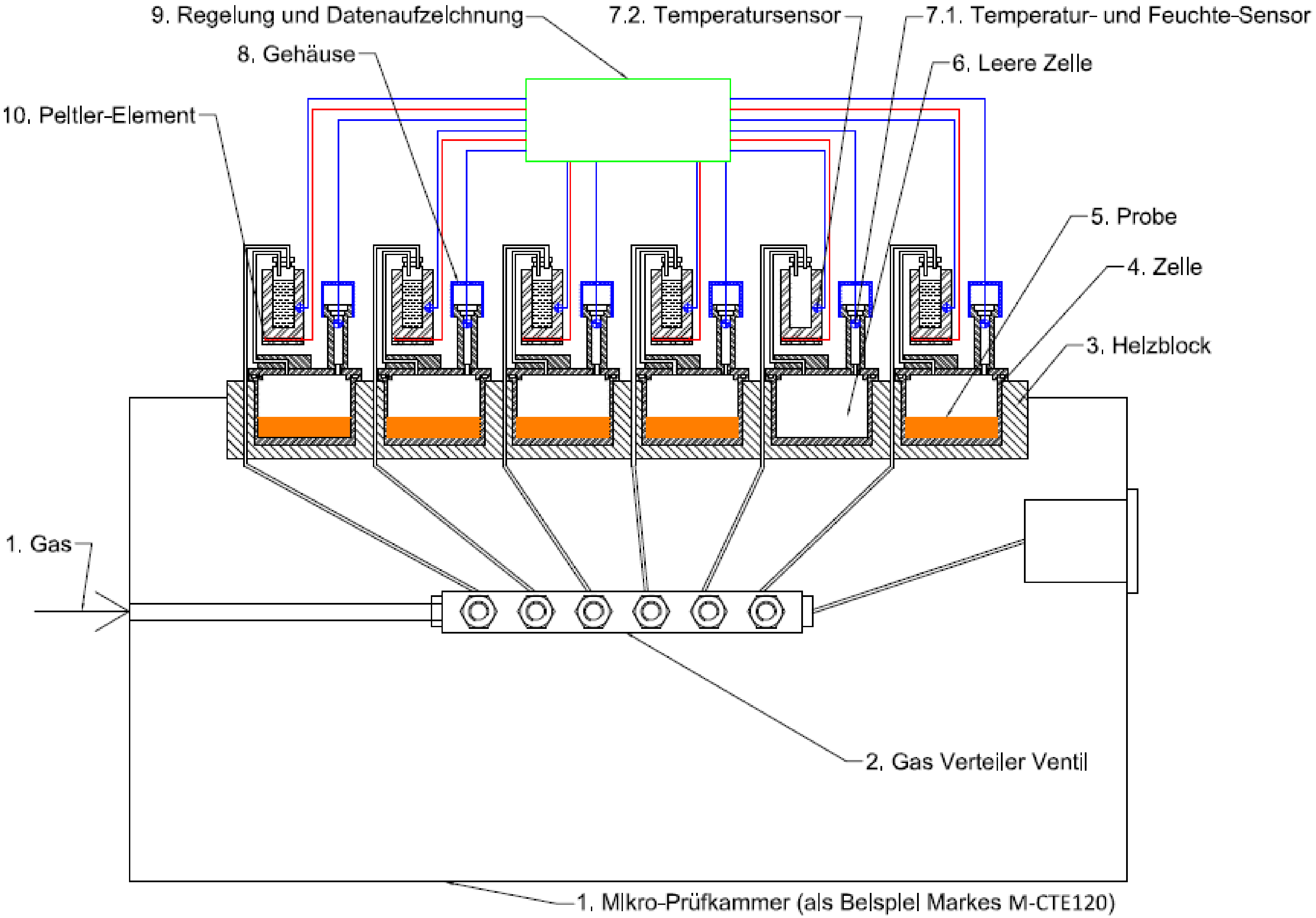


Figure 38. Individual humidity control system (Stratev and Srebotnik) for micro-chamber (Humidifier)

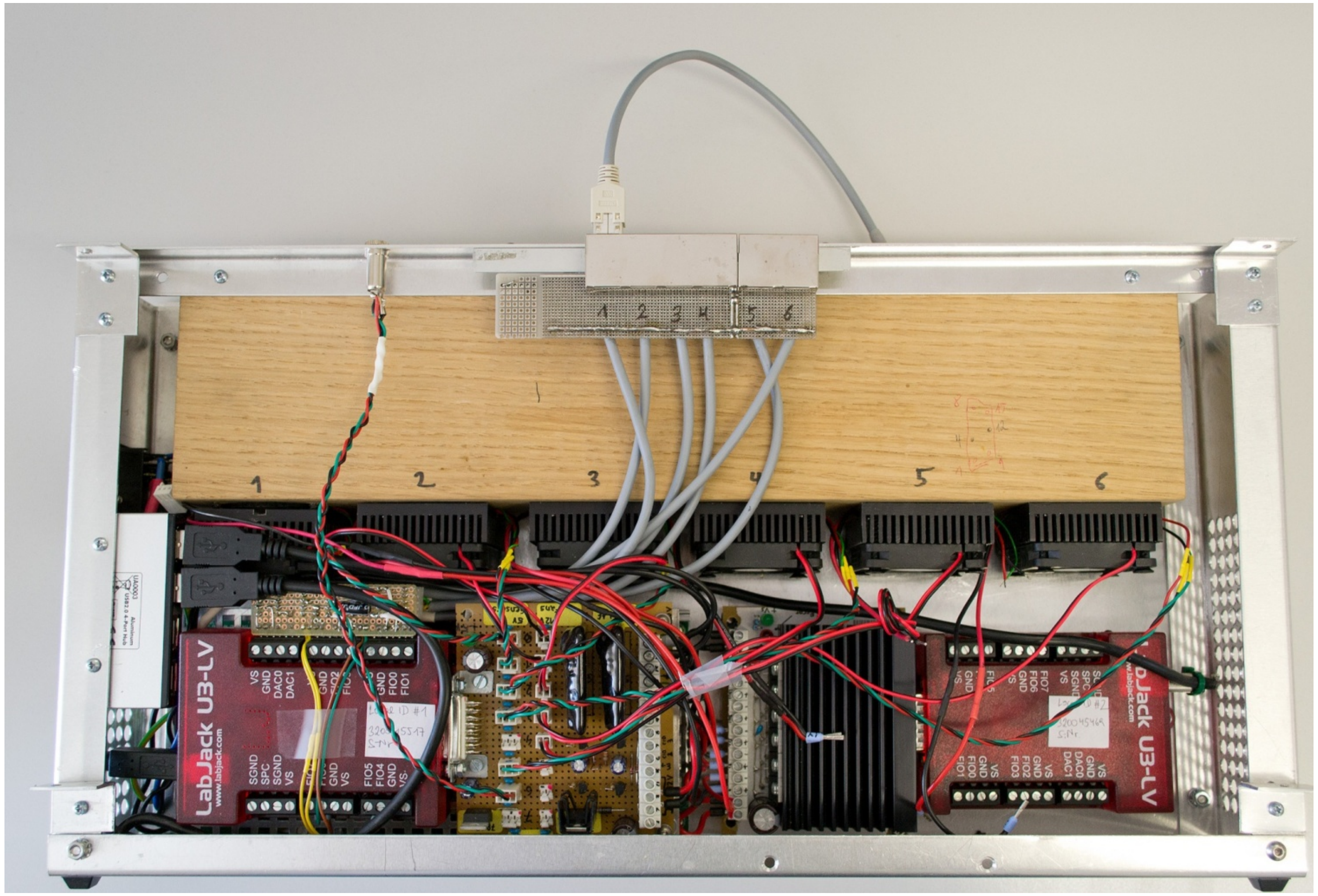


Figure 39. Prototype of Humidifier/Evaporator – Stratev and Srebotnik

9.4.4. Edge effect interferences

The initial idea behind this experiment was the quantification of the VOC edge (cut surface) emissions of OSB made of pine-wood. For the purpose the test depicted on Figure 40 was conducted. The samples were cut in a half in order the initial differences in respect to VOC emissions between the two compared groups to be minimal. The curved edges of all samples were sealed with 3M aluminum foil tape. Five samples with unsealed diametric cut surfaces formed the group of the "not sealed" samples. The corresponding five halves with sealed diametric edges formed the group of the "sealed" samples. There was also a sample which was completely sealed with aluminum foil tape and was supposed to be the negative control sample.

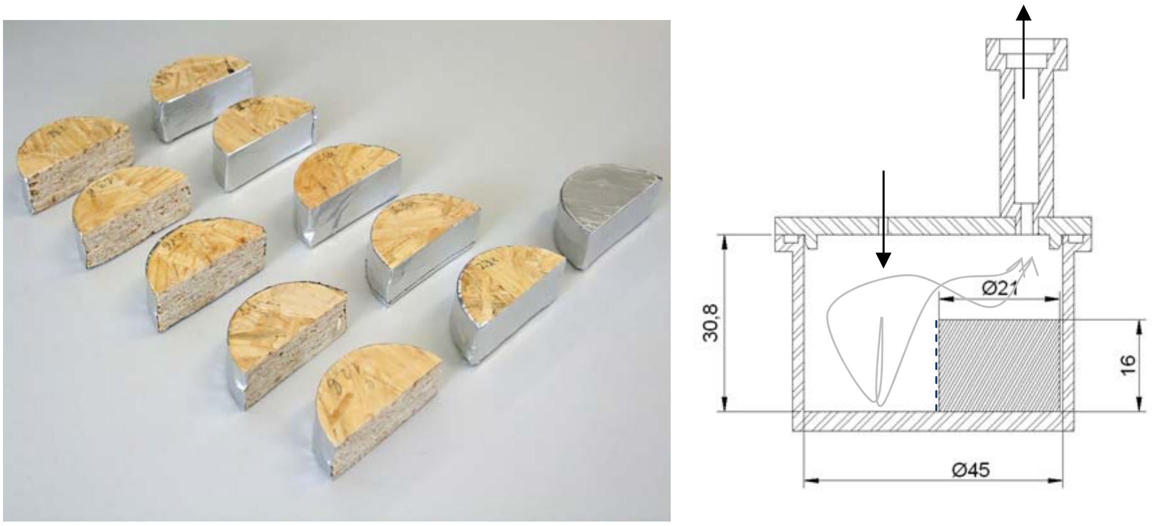


Figure 40. Experimental setup for examination of the edge effects on VOC emissions

The conditions in the micro chambers are given in Table 6 and the results for the lead substances are presented on Figure 41.

The biggest surprise was that the negative control sample did not behave as such and in some cases (α-pinene) the VOC emissions were higher than the unsealed samples.

If only terpenes' emissions (primary VOC - 9.1) are observed, it seemed like there are two mechanisms of VOC transport inside the sample. The first mechanism (gaseous diffusivity) is hindered from the foil sealing and the terpenes could not evaporate from the sample at high rates. The unsealed samples lose their terpenes at much higher rate in the beginning of the experiment or even before the samples are put into the cells (unfortunately this was not confirmed with measurements since the first sampling took place at day three). The sealed samples lose their terpenes at lower rates at the beginning (also not supported by measurements).

Table 6. Experimental conditions

Experiment name	OSB13
Sample type	OSB
n	2x5+1
Sample height [mm]	16
Experiment duration [days]	14
Sample diameter [mm]	42
Average temperature [°C]	23
Average relative humidity [%]	50
Technical air flow rate [ml/min]	19.5

At certain time point the unsealed samples reach a state at which the decrease of their terpenes emissions is slowed down. The same takes place by the sealed samples at a later stage and the foil is not throttling the VOC transport anymore because the bottleneck is the VOC transport inside the samples.

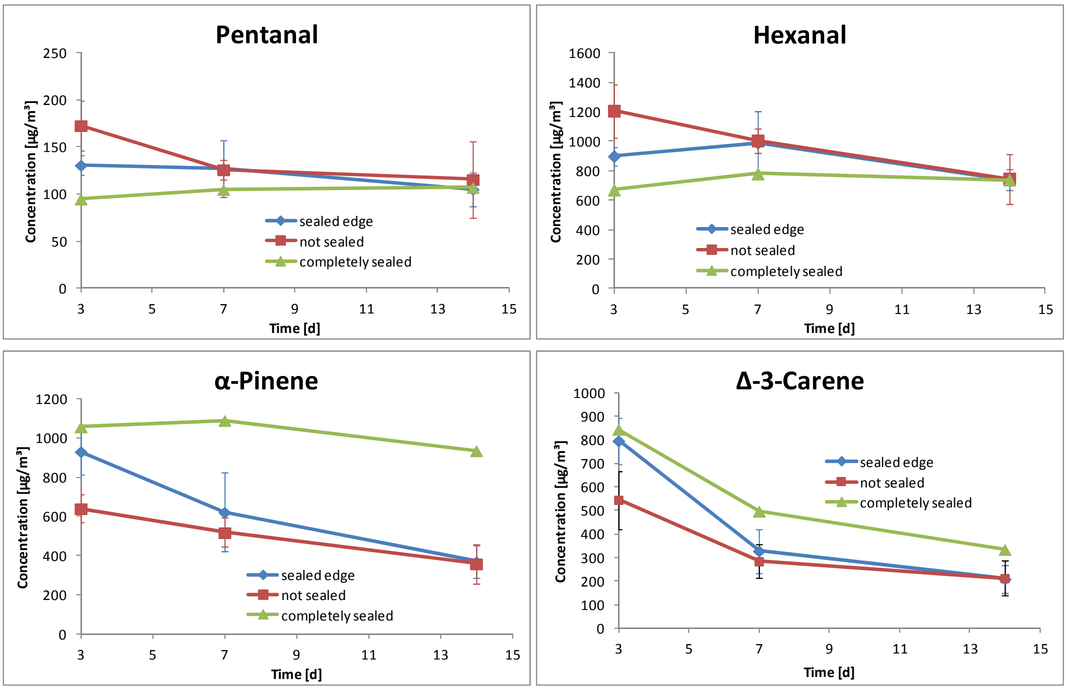


Figure 41. VOC emissions from OSB samples with sealed and non-sealed edges

The completely sealed “negative control” sample emits α-pinene at a constant maximum rate till the end of the experiment. This hints that the internal transport has the capacity to deliver enough α-pinene to the surface (at least to the edge-surface) and the sealing is creating a bottleneck.

By the secondary emissions the situation was reversed: The more surface-area was sealed the lower the aldehydes emissions were. The author supports the opinion that this occurrence does not take place as a result of selective aldehydes’ transport hindrance by the sealing tape but rather as a result of the different terpenes concentrations inside the samples. It seems like monoterpenes with their high partial pressures in the sample cavities have preventive effect on UFA oxidation hence aldehydes formation. Similar occurrence was observed in other experiments (10.2) where the dilution of both terpenes and UFA in the end-product only led to a reduction in the terpenes emissions but not in the aldehydes emissions.

9.4.5. Exploring the VOC permeability of different sealing materials

Permeability of sealing materials in the context of IAQ evaluation is important because of the following reasons:

- The majority of the IAQ-standards describe the usage of proper packaging for transport and storage of test specimens till being analyzed, but it is often not specified which material is suitable;
- Sealing of test specimens' cut surfaces should be often applied and if the sealing material is permeable this could lead to misinterpretation of the results;
- Sealing of cut surfaces with impermeable materials is very important for small-scale measurements since the proportion cut-surface to "normal" emitting-surface is much higher (9.3.3).

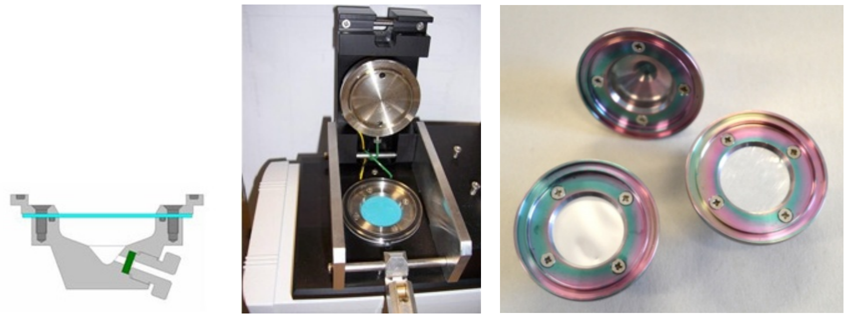


Figure 42. Tool for measuring VOC permeability of different sealing materials with the help of µCTE

With the help of the adaptor shown on Figure 42 the gaseous permeability of different sealing materials was explored. Initially it was done for water vapor by filling the vessel with water and measuring the humidity above the permeable membrane (for 30 minutes) and by supplying dry air to the micro chambers (Table 7).

Table 7. Estimation of water - vapour permeability of different sealing materials

Sealing material	Relative humidity
Water without membrane	93 %
Isover Vario KM Duplex	28 %
aluminum adhesive foil 3M-425	1.4 %
PE foil - freezer bag	0.8 %
Allpax vacuum foil VAS-1220 PA/PE	0.6 %
aluminium laminated bag (12µ PE/12µ Al/75µ LDPE)	0.2 %

Similar experiments were conducted with an aldehydes and terpenes mixture which was injected in the vessel and the TVOC concentrations above the membranes were determined (for a period of 28 days) with the standard Tenax-GC/MS analytics (results are shown Figure 43).

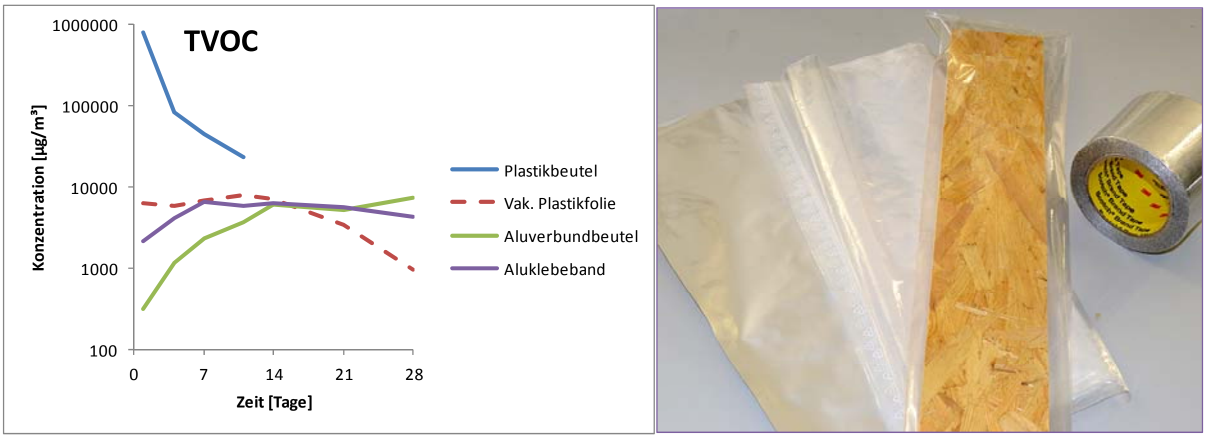


Figure 43. VOC permeability of different packaging foils

Both experiments show that there are vast differences in the permeability-properties of the different sealing materials and their usage should be selected critically.

The unusual high concentrations of analytes below the membranes of interest could be pointed to be drawback of this experimental approach because in some cases the analytes tended to condensate on the internal side of the membrane thus creating additional layer for permeation. Therefore, the usage of well characterized matrix (like softwood flour) is recommended if further experiments will be conducted.

9.4.6. Remarks about the usage of suitable cutting technique for µCTE-samples

Another interference factor which could be easily neglected is the choice of a proper sample cutting technique. The cutters used for sample preparation should be cleaned from lubricating oil residues through dipping in suitable solvents like high purity acetone or/and hexane. Thermal load which is introduced with the friction with the metal during cutting can intensify the oxidative reactions in the cutting region (Figure 44) and can severely affect the following VOC emissions evaluation. Artifact substances produced as a result of cutting could be emitted in high concentrations and could contribute for a negative product evaluation. Some authors recommend the usage of liquid nitrogen or dry ice for reducing thermal load. Since this could lead to condensation of air moisture (if cutting is done under normal conditions) the author of this work recommends the usage of hard metal hole-cutters. Very convenient for cutting out OSB- (or CLT-) samples for the µCTE was the “HM Mehrzweck-Lochsäge Bohrkrone Wolfcraft 3782000 Ø 45” in combination with the Bosch PBD 40 bench drill.

A positive side effect when using metal hole-cutters with softwood is the production of sizeable amount of wood flour (Figure 44). It can be used without further preparation for extractives analysis.

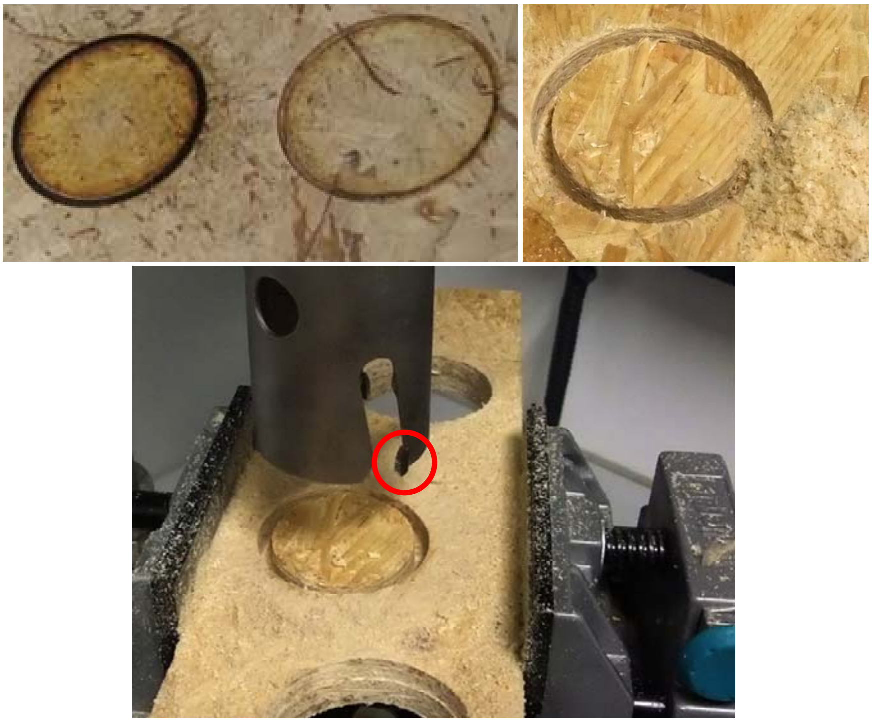


Figure 44. Influence of the thermal load during cutting out samples for the µCTE. Above from left to right: bi-metal hole saw without cooling intervals, bi-metal hole saw with cooling intervals, hard metal hole cutter without cooling intervals. Below: HM Mehrzweck-Lochsäge Bohrkrone Wolfcraft 3782000 Ø 45

9.4.7. UV and ozone

µCTE could be easily modified for exploring the influence of UV and ozone on building materials. The integration of UV-LEDs and the enriching of air supply with ozone were considered by the author but because of time limitations were not implemented. Analytics based on BPE-DNPH like this described in 9.2.2 could be used for determining and adjusting the applied ozone concentrations.

9.4.8. Determination of VOC diluted in aqueous solutions

By using elements from the humidity control system described in 9.4.3 the author constructed a small-scaled purge and trap installation which was suitable for analysis of VOC diluted in aqueous solutions like dry-kiln condensates (Figure 45).

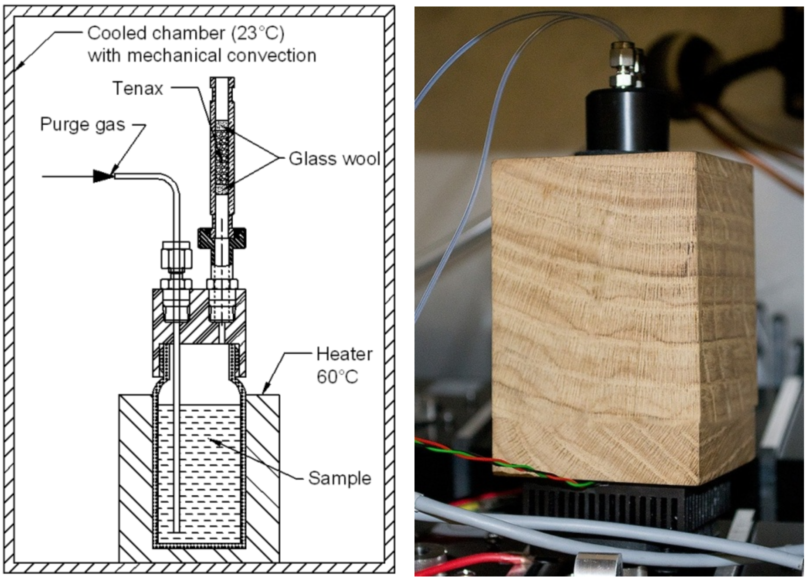
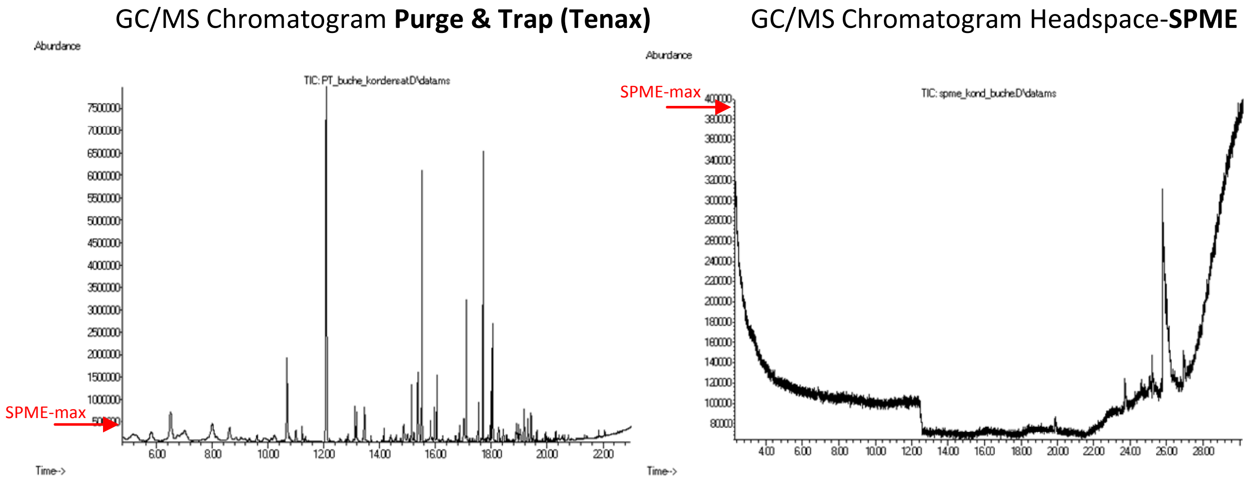


Figure 45. Laboratory purge and trap installation constructed by using elements of the µCTE humidity control system

By using this analytics an extensive overview of the volatile constituents of three dry-kiln condensates (spruce, spruce/pine and beech) was done (Rathke, Stratev 2013). A later publication completed the topic by also covering the nonvolatile dry-kiln condensates (Stratev et al. 2015b).

In the course of this research it was shown that the classical liquid-liquid extraction of the extractives (like for example MTBE-extraction) or Headspace-SPME techniques was not suitable for determination of VVOC/VOC in dry-kiln condensates, because of the low concentrations of the analytes (Figure 46).



GC/MS Chromatogram **Purge & Trap (Tenax)**

GC/MS Chromatogram Headspace-**SPME**

Figure 46. Comparison between two techniques for VOC determination in aqueous solutions

10. Methods for VOC*-emissions reduction

10.1. Overview

In order to reduce VOC-emissions from softwood engineered softwood-based products the producer could use one (or a combination) of the following techniques:

- (Partial) Extraction of the VOC and their precursors containing in the material
- (Partial) Substitution of the VOC-emitting raw material with VOC-inert raw material
- Addition of scavengers in order to absorb emitted VOC*
- Addition of antioxidants in order to inhibit the formation of secondary VOC (9.1)
- Decomposition of VOC or their precursors through oxidation and formation of VVOC (or another VOC)
- Biological (microbial) or enzymatic treatment of the raw material in order to selectively metabolize or decompose VOC or their precursors

The author was involved in experiments with softwood which covered some of the topics above and the next paragraphs will shortly describe the outcomes of this work.

10.2. Mixing of different wood arts (pine-poplar)

In this experiment (Kuncinger, Stratev) poplar was used for the substitution of 50 weight percent of the raw pine which is normally used by the production of OSB.

Three types of laboratory boards with thickness of approximately 11 mm and density of approximately 790 kg/m^3 were produced. The first two types were the control samples consisting of 100% pine and 100% poplar and the third type was the 1:1 (w/w) mixture. Four cut outs with diameters of 42 mm of each type were exposed for 14 days in µCTE micro chambers at standard conditions (23°C, 50%RH) and the VOC were characterized with Tenax-GC/MS-analytics. The results of the experiment are given in Table 8.

Table 8. Substitution of pine with poplar by the production of OSB (Stratev-Kuncinger): I (K) – OSB from 100 % Pine; II (P) – OSB from 100% Poplar; III (KP) – OSB from 50:50 (w/w) Pine/Poplar

VOC	**Day 3**			**Day 14**		
	I (K) **[µg/m^3]**	II (P) [% from I]	III (KP) [% from I]	I (K) **[µg/m^3]**	II (P) [% from I]	III (KP) [% from I]
Pentanal	28	<1%	**74%**	34	<1%	**86%**
Hexanal	224	6%	**67%**	275	3%	**77%**
α-Thujene	56	<1%	50%	19	<1%	37%
α-Pinene	3654	1%	**43%**	1398	1%	**48%**
Camphene	35	<1%	34%	14	<1%	32%
m-Cymol	43	<1%	57%	20	<1%	19%
β-Pinene	1170	<1%	**22%**	534	<1%	**14%**
Pentylfuran	19	<1%	84%	15	<1%	57%
Octanal	16	28%	61%	16	84%	96%
β-Myrcene	69	0%	59%	38	<1%	29%
Δ3-Carene	3954	1%	**55%**	1054	1%	**48%**
o-Cymol	70	<1%	49%	26	<1%	29%
Limonene	80	<1%	**95%**	28	<1%	**76%**
2-Octenal	+	-	**appr** . 50%	7	<1%	**53%**
Nonanal	37	31%	72%	35	66%	80%
α-Terpinolene	105		67%	35	<1%	65%
Decanal	32	42%	84%	41	71%	65%
Dodecane	4	420%	197%	14	10%	52%
Longifolene	14	<1%	125%	16	<1%	24%

The results of the experiment show that laboratory made OSB consisting from 100% Poplar were very low emitting when compared to pine-based OSB. Laboratory made OSB from 50:50 mixture of pine and poplar emitted approximately the half of the monoterpenes of the pine-based OSB but 80-90% of the characteristic aldehydes like pentanal or hexanal. It is of interest whether this behavior would have been also observed after longer time periods (≥28 days).

Just like in another experiment of the author (9.4.4) the reduction of the terpenes concentrations inside the panels led to increase in the aldehydes production.

10.3. Reducing agents (DiBAL $NaBH_4$)

The subject of this experiment (Stratev) was to test the influence of strong reducing agents like DIBAL-H and $NaBH_4$ on the VOC emissions from pine-wood particles. The time of the experiment was limited to 28 days and the VOC emissions of the pine wood particles were characterized with headspace SPME – GC/MS. The peak areas (without internal standard correction) were used for gaining idea for the change in the VOC concentrations of the lead substances (in the SPME vials). Two characteristic chemical groups with the following lead substances were examined:

- Aldehydes – Pentanal, Hexanal
- Monoterpenes – alpha-Pinene, beta-Pinene and delta-3-Carene

It is known that strong reducing agents are capable of converting aldehydes to alcohols (Miller et al. 1959). This experimental setup was a proof of concept in order to verify whether the reaction of the reducing agents with aldehydes and their precursors (UFA) would lead to a reduction of the aldehydes' emissions.

The following reagents were used: 100 µl of 1M DIBAL-H in CH_2Cl_4 and of $NaBH_4$ in ethanol.

Approximately 1% (w/w) DIBAL-H respectively $NaBH_4$ solutions were added to 1 g dried pinewood particles and the VOC-concentrations in the headspace of the vials were estimated through SPME/GC-MS measurements for a period of 28 days. The addition of the reductive solutions took place under anaerobic conditions and the first ventilation took place 7 days after the start of the experiment.

Table 9. Testing procedure of the experiment (Reducing agents)

Time [days]	Note
0	Start
3	SPME_3d
7	SPME_7d
7	Ventilation for 10 sec
14	SPME_14d
14	Ventilation for 5 min
28	SPME_28d

The treatment of pinewood particles with reducing agents led to the complete elimination of the typical (for products based on pinewood) aldehyde emissions. Unexpectedly the emissions of monoterpenes of the samples treated with $NaBH_4$ were also significantly reduced (Figure 47).

Non-characteristic (for pinewood) volatiles, like ethyl acetate, butanol ($NaBH_4$-treatment) or isobutan (DIBAL-H-treatment), were detected in the vials with treated samples (results not shown).

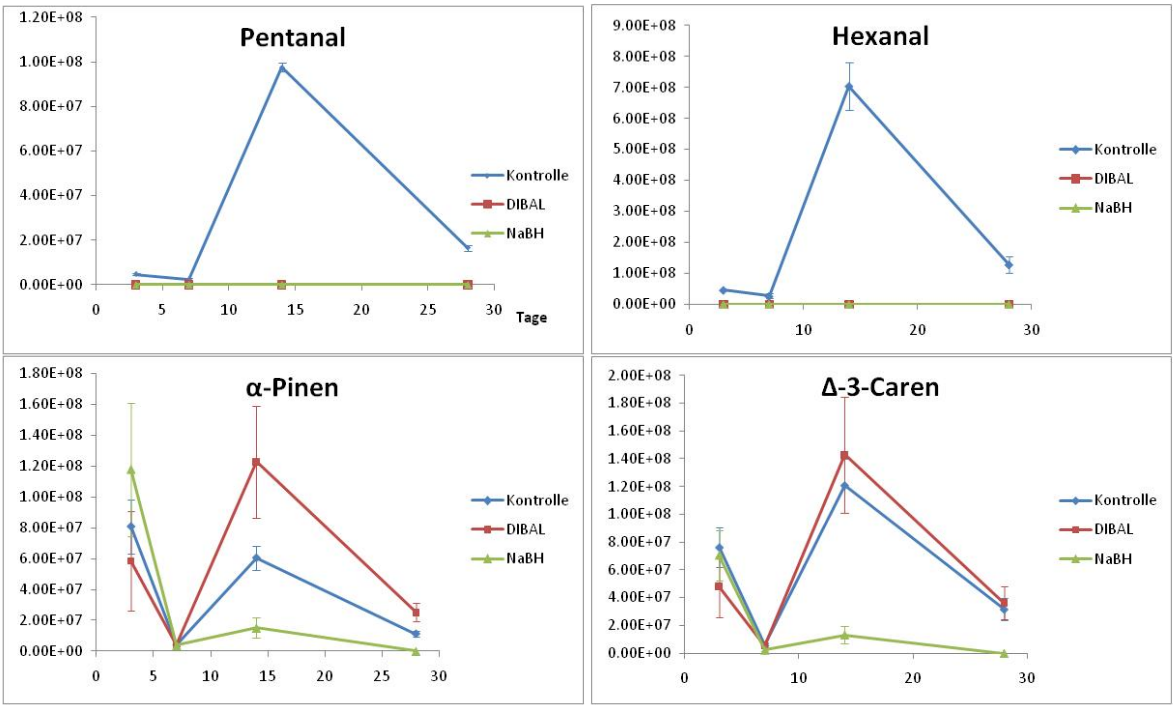


Figure 47. VOC emissions from wood particles samples treated with reducing agents (DiBAL NaBH4)

10.4. Scavengers

Similar approach as the above but conducted with scavengers (1% and 10% w/w β-cyclodextrine were added to the softwood particles) did not lead to significant reduction in the emissions of any of the observed aldehydes or monoterpenes (results are not shown).

10.5. Microbial treatment of the raw material in order to selectively metabolise or decompose VOC or their precursors

10.5.1. Fungal treatment

The following peer reviewed articles of Stratev et al. indicate that blue staining fungi which are considered to be non-destructive for pinewood are capable of metabolizing aldehyde precursors. (Stratev et al. 2009) (Stratev et al. 2011) (Weigl et al. 2015a) As results aldehyde emissions of treated samples (resp. products) are significantly reduced.

10.5.2. Bacterial treatment

The following peer reviewed article indicates that bacteria are also capable of metabolizing aldehydes precursors and reduce aldehydes emissions from products based on pine-wood (Stratev et al. 2016b).

10.5.3. Conclusion microbial treatment

Both fungal and bacterial treatment of softwood led to a significant reduction in the aldehyde emissions from laboratory made plates. However, treatment was conducted by using sterilized raw material and under controlled conditions like material humidity and temperature of cultivation. In another experiment where unsterile conditions and no temperature control was used (results not shown) the products based on treated material showed no significant differences with the control samples in respect to their aldehyde emissions.

It should be pointed out that microbial treatment of pinewood could be considered as controlled and accelerated seasoning of the raw material by which no unpredicted coloration effects or significant worsening of the product’s mechanical properties occurs. By the natural seasoning process the development of characteristic microbiota certainly also leads to reduction in the concentrations of unsaturated fatty acids hence of aldehyde emissions. However it cannot be ruled out that coloration effects occur due to the settlement of blue stain fungi in the softwood material.

Some stumbling blocks by the isolating and the usage of bacteria as agents for reducing the concentrations of unsaturated fatty acids (UFA) in softwood are the species determination and the further cultivation of the suitable strains in the laboratory. The author and his team used mainly API-20 tests for species determination and standard media (malt extract agar) for bacteria cultivation. However, both approaches were suboptimal because the certainty of species determination was often not high enough and the isolated strains could not be cultivated on standard media longer than a few days. The author highly recommends the combination of API and PCR for species determination as well as the usage of selective media (based on the identification results) for the further cultivation and storage.

10.6. Enzymatic treatment

Experiments conducted and described from another author in the same team (Ters 2015) indicate that selected fungal enzyme extracts are capable of degrading UFA containing in finely milled wood. However, the same enzyme concentrates are not capable of degrading UFA in wood materials with intact ultra-structure (wood cells) most probably because of steric effects (enzyme molecules are too big and cannot reach and degrade UFA).

10.7. Steam extraction of primary VOC in order to reduce further emissions

This paragraph is called steam extraction of primary VOC in analogy to the steam distillation used by the extraction of flavors and fragrances. In the case of wood panels production, the condensation step is not an obligatory step, but could be profitable since the typical primary softwood VOC are the same fragrances used in the cosmetics-, washing agents- and other industries.

Drying of wood particles (or strands) to certain moisture content is critical for their further pressing and gluing into wood panels. As soon as the proper moisture content is reached the drying process should be discontinued in order an optimal performance during the pressing- and gluing- stage to be achieved. Since primary VOC expel from the wood material correlates to the energy which is introduced during the drying process it is obvious that primary VOC could be further extracted from the wood material (even after reaching optimal moisture content) only if sufficient water (steam) is reintroduced to the system (in order to compensate for the moisture evaporated from the material). Steam could be also introduced during the drying step (in parallel to the dry air) thus lowering the efficiency of the drying and prolonging the interval in which primary VOC could evaporate and leave the system (Figure 48). An increase of the initial strands' moisture content like for example during microbial treatment (10.5.3) could have similar effect.

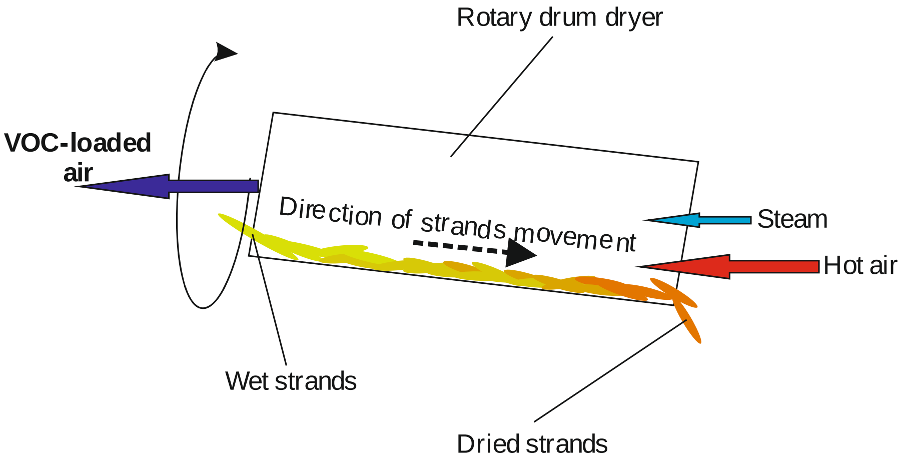


Figure 48. Schema of steam extraction of primary VOC

Although the implementation of this idea is not very challenging, due to time limitations the author was not able to conduct any experiments in this direction.

10.8. Oxidation of aldehyde precursors (with ozone, UV ect.)

Ozone treatment and UV irradiation are known to be capable of initiating autoxidative degradation of UFA. Therefore, their usage at the (pre)production stage should also be considered in order UFA content and aldehydes emissions to be better controlled. The author did not conduct experiments in this direction but as mentioned above (9.4.7) the µCTE chamber is a convenient tool for this purpose.

11. Retention indices for VOC emitted from softwood based products

In the gas chromatography in cases where the retention times of the compounds are compared to the retention times of ubranched saturated alkane-homologues it is much more common to use the so called retention indexes (RI) than the retention times. By deffinition (Kováts 1958; IUPAC 2009; Agilent Technologies Inc. 2007) the ubranched saturated alkane-homologues have RI equal to the number of their C-atoms multiplyed by 100 (methane - 100, ethane - 200,...,hexadecane - 1600, etc.). The advantage of declaring RI instead of RT is that the first is almost independent of the parameters of chromatographic system like temperature programm or column length and is only dependent of the type of the selected stationary phase. There are many databases with retention indexes for many substanses on different stationary phases (chromatographic columns) but the most comprechensive public available database which the author has used is the NIST database (NIST Mass Spec Data Center').

For evaluation schemes (like AgBB) which use alkanes and their retention times as base for differentiating the volatility of the compounds it is very easy to redefine the subgroups. In such cases VOCs could be defined as these compounds with retention indexes between 600 and 1600 on an apolar capilar GC column. Analogously SVOCs schould be these volatiles with RI between 1600 and 2200 and VVOCs should be the substances with RI < 600.

Normally the retention indexes are correlating to the vapour pressures (hence to the boiling temperatures) of the volatile compounds. However due to the apolar properties of the specified (ECA-IAQ 1997a) stationary phase of the GC-column some deviations for polar volatiles are obsereved because they hardly interact with column’s stationary phase and tend to elute earlier as apolar volatiles with similar vapor pressures (boiling points). Because of such phenomena the acetic acid could be somethimes categorised as VVOC to which group it ceirtanly does not belong when consierating its vapour pressure at 20°C.

During his work with the HP Pona chromatographic column (Agilent 19091S 50 m x 0.2 mm i.d. x 0.5µm by using a temperature ramp program) the author was able to determine the retention indices of more than 100 VOC and the majority of them can be related to softwood products (Table 10).

Table 10. Retention indices for VOC emitted from softwood based products determined on an Agilent HP-Pona column and calculated (Agilent Technologies Inc. 2007) for a temperature ramp program of the oven

VOC	CAS number	RI
Butanol	71-36-3	646
Benzene	71-43-2	653
Cyclohexane	110-82-7	653
Dimethylsilanediol	1066-42-8	654
1-Methoxy-2-propanol	107-98-2	658
Nitric acid, 1-methylethyl ester	1712-64-7	662
Trioxane	110-88-3	667
2-Pentanon	107-87-9	668
Propanoic acid	79-09-4	668
Pentanal	110-62-3	676
Heptane	142-82-5	700
Formic acid, butyl ester	592-84-7	710
2-Methyl-4-pentanone	108-10-1	720
Dimethylformamide (DMF)	68-12-2	733
Pentanol	71-41-0	749
Toluol-D8 (IST)	2037-26-5	755
Toluol	108-88-3	759
Hexanal	66-25-1	781
Octane	111-65-9	800
Furfural	98-01-1	810
Possible 2-Hydroxy-2-methyl-4-pentanone (Diacetone alcohol)	123-42-2	814
Hexamethylcyclotrisiloxane	541-05-9	817
2-Hexenal	6728-26-3	837
Ethylbenzene	100-41-4	856
1-Hexanol	111-27-3	852
Xylene I	1330-20-7	864
Xylene II	1330-20-7	865
Cyclohexanone	108-94-1	872
2-Heptanone	110-43-0	873
Butylether	142-96-1	879
2-Propenoic acid, butyl ester	141-32-2	883
Heptanal	111-71-7	883
2-Butylfuran	4466-24-4	886
Xylene III	1330-20-7	888
2-Butoxyethanol	111-76-2	890
Propanoic acid, butyl ester		896
Nonane	111-84-2	900
2-Heptenal	18829-55-5	935
α-Pinene	80-56-8	940
Benzaldehyde	100-52-7	942
Hexanoic acid	142-62-1	944
Camphen	79-92-5	951
Possible n-Butyl methacrylate	97-88-1	962
3-Octanone	106-68-3	969
2-Octanone	111-13-7	972
Sabinen	3387-41-5	974
β-Pinene	127-91-3	982
Butyl butanoate	109-21-7	983
2-Pentylfuran	3777-69-3	986
Octanal	124-13-0	985
cis-p-Menth-8-ene	1879-07-8	987
β-Myrcene	123-35-3	987
Dimethyl succinate	106-65-0	995
Octamethylcyclotetrasiloxane	556-67-2	996
Decane	124-18-5	1000
2,2,4,6,6-Pentamethylheptan	13475-82-6	1001
alpha-Phellandrene	99-83-2	1004

Possible 2-Ethyl-1-hexanol	104-76-7	1014
Isocineol	470-67-7	1015
Δ3-Carene	13466-78-9	1018
α-Terpinene	99-86-5	1018
p-Cymol	99-87-6	1023
Limonene	138-86-3	1032
Eucalyptol	470-82-6	1035
1,2-Diethylcyclohexane	824-43-1	1036
Cyclohexanol, 3,3,5-trimethyl-, trans-	767-54-4	1039
2-Octenal	2548-87-0	1041
Possible 2,2,4,4-Tetramethyloctane	62183-79-3	1044
Cyclohexanol, 3,3,5-trimethyl-, cis-	933-48-2	1047
Acetophenone	98-86-2	1050
γ-Terpinene	99-85-4	1060
Methyl benzoate	93-58-3	1081
Possible p-Cymenene	1195-32-0	1085
Nonanal	124-19-6	1088
Fenchone	1195-79-5	1088
α-Terpinolene	586-62-9	1090
Unknown glass wool artifact RI1090		1090
Pentanedioic acid, dimethyl ester	1119-40-0	1099
Undecane	1120-21-4	1100
α-Pineneoxide	1686-14-2	1103
Fenchol	1195-79-5	1119
Isofenchol	2217-02-9	1119
Possible α-Campholenal	4501-58-0	1123
Camphor	76-22-2	1143
Cyclodecen	935-31-9	1148
Decamethylcyclopentasiloxane	541-02-6	1156
Cyclodecane (IST)	293-96-9	1159
Pinocamphone	547-60-4	1161
p-Cymen-8-ol	1197-01-9	1169
Isopinocamphone		1177
Terpinen-4-ol	562-74-3	1180
Possible α-Terpineol	98-55-5	1190
Decanal	112-31-2	1190
Estragol	140-67-0	1191
Dodecane	112-40-3	1200
Verbenone	80-57-9	1205
p-Isopropylbenzaldehyde	122-03-2	1213
Fenchyl acetate	13851-11-1	1224
Possible Siloxane_RI1230		1230
Possible Siloxane_RI1237		1237
2-Decenal	3913-81-3	1247
2,4-Decadienal	25152-84-5	1280
Bornylacetate	76-49-3	1288
Undecanal	112-44-7	1293
Tridecane	629-50-5	1300
Iso-2,4-Decadienal	25152-84-5	1301
Butoxyethanol acetate	124-17-4	1337
Possible α-Longipinene	5989-08-2	1378
Tetradecane	629-59-4	1400
C15H24 RI1400		1405
Longifolene	475-20-7	1442
Isolongifilen	1135-66-6	1443
Pentadecane	629-62-9	1500
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	74381-40-1	1597

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Appendix II Relevant articles in peer-reviewed journals and non scholar sources with Stratev as first author or co-author

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