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VOC Emissions from building materials - the impact of specimen variability - a case study.

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ABSTRACT

Significant progress has been made in the development of standardized methods for the testing and analysis of volatile organic compound (VOC) emission characteristics of different building materials. These standardized techniques facilitate product-product comparisons with regard to VOC emissions, and also provide a basis with which to examine the impact of environmental conditions on VOC emissions. Variability of the test specimen itself is one factor that must be considered when evaluating such tests. In an attempt to gauge this effect, a series of samples of oriented strand board (OSB) were collected and subjected to chamber tests for VOC emissions under standardized conditions (23°C, 50% RH, 1 air change per hour, 0.4 m²/m³ loading). Specimens were collected directly from the mill sites of three different manufacturers. Repeat samples were also collected from the same retail outlet on three separate occasions (same manufacturer, 3 different production dates), from separate panels produced on the same production date, and from multiple locations within the same panel. Variability in the VOC emissions from these samples was found to exceed the analytical uncertainty by an order of magnitude in certain cases.

INTRODUCTION

Testing of chemical emissions from building materials is increasingly conducted to assist with the design, construction and renovation of buildings so as to provide optimal indoor environments.¹ The growing number of labeling schemes which attempt to rank products based on their VOC emissions,^{2,3,4} and of databases seeking to catalog emission test results,^{5,6,7,8} underscores the need for reliable, standardized testing protocols.⁹ Several detailed guidance documents are currently available to describe such tests,^{10,11} but by definition, their recommendations are non-mandatory and consequently, many reported test results are neither repeatable nor comparable. Strict procedures for, and documentation of, specimen collection, handling, conditioning, and chamber characterization/operation are vital, as are precise control of VOC sampling and analysis techniques in maximizing uniformity and comparability of reported emissions data. Efforts to meet these challenges continue.^{12,13,14,15}

Even if such tight control of testing procedures is achieved, some variability in the observed chemical emissions for a given building material is still to be expected.¹⁶ Material in-homogeneity is at least partially blamed for some of the inconsistent results obtained in several recent round robin lab evaluations.^{17,18} Variability in the raw materials used in manufacture, and in the manufacturing processes themselves leads to non-uniformity in the emission characteristics of many building materials. OSB, widely used in the construction industry, is one example of a product which is relatively in-homogeneous. OSB is a complex mixture of a

variety of wood species (typically aspen-poplar or yellow birch), phenol-formaldehyde resins (or equivalents) and waxes. A variety of mechanical techniques and processing conditions are employed in the manufacture of the panels. In a study on the impact of furnish drying temperature, moisture content, panel pressing time, pressing temperature and resin content on VOC emissions from OSB panels, drying temperature in particular was found to have a significant impact on VOC emissions from the finished material.¹⁹

A series of tests of OSB were conducted, under carefully controlled conditions, to examine the degree of variability that can occur in the emissions of VOCs from a single building product. This comparison is material-dependent, but has general impact on the manner in which emission results are presented and on the way in which emissions databases and material labeling schemes rate their inventories.

EXPERIMENTAL METHODS

Specimen Selection and Handling

OSB specimens were obtained from a variety of sources (summarized in Table 1). Specimens 1, 2 and 3 were collected directly from mill production sites under strict quality control procedures.¹³ Specimens 4 through 7 were all purchased from a large retail outlet close to the testing lab. For each of these specimens, an OSB panel near the center of an undisturbed stack of panels was collected along with the two immediately adjacent panels (which were clamped together with the test panel to form a protective sandwich). On receipt at the lab, 112 by 212 mm test specimens were immediately cut from the panel with a clean saw (using the sandwich panels as work surfaces) and stored in clean sample bags; flushed with zero-grade air, and stored at 23°C for a minimum 48 hours prior to chamber testing. The cut dimensions of the specimens are provided in Table 2. Immediately prior to chamber testing, the specimens were placed in an electropolished stainless steel holder.¹³ The holder served to restrict the emitting surface of the specimen to an area of 100 x 200 mm, and also prevented emissions from the side and bottom faces of the specimen. For samples 4 through 7, the “this side down” face of the panel was exposed to the chamber, since in typical residential construction; this would be the primary exposed surface (looking up at the exposed sub-floor from the basement).

Table 1. Specimen description.

Test Code	Nominal Thickness, mm / Application	Origin	Manufact. - Test Lag, d	Location in Sheet	Comments
OSB1	12.7 / Grade R-1 Sheath	Mill A	9	center	Collected on day of manufacture
OSB2	11.1 / Grade O-2 Sheath	Mill B	9	center	Collected 3 d after manufacture
OSB3	15.9 / Grade O-2 Sheath	Mill C	6	center	Collected 1 d after manufacture
OSB4	14.5 / T&G Sub-Floor	Mill B /Retail	57	center	
OSB5a	14.5 / T&G Sub-Floor	Mill B /Retail	25	P1 corner	1 st of 4 samples from single sheet
OSB5b	14.5 / T&G Sub-Floor	Mill B /Retail	25	P5 center	2 nd of 4 samples from single sheet
OSB5c	14.5 / T&G Sub-Floor	Mill B /Retail	25	P5 center	3 rd of 4 samples from single sheet
OSB5d	14.5 / T&G Sub-Floor	Mill B /Retail	25	P9 corner	4 th of 4 samples from single sheet
OSB6a	14.5 / T&G Sub-Floor	Mill B /Retail	41	P1 corner	1 st of 4 samples from 2 sheets
OSB6b	14.5 / T&G Sub-Floor	Mill B /Retail	41	P5 center	2 nd of 4 samples from 2 sheets
OSB7a	14.5 / T&G Sub-Floor	Mill B /Retail	41	P1 corner	3 rd of 4 samples from 2 sheets
OSB7b	14.5 / T&G Sub-Floor	Mill B /Retail	41	P5 center	4 th of 4 samples from 2 sheets

Chamber Testing

Four identical electropolished stainless steel chambers with internal volumes of 0.050 m³ were used in this study according to the guidelines of ASTM D5116.¹⁰ Chamber conditions for all tests were 23°C, 50% relative humidity and a nominal air change rate of 1.0 h⁻¹ (~1.04 h⁻¹ after correction for volume occupied by the specimen and specimen holder). Mass flow controllers regulated the chamber supply air from an Aadco pure air generator which was humidified to 50% RH with HPLC grade water. This system produced clean air with TVOC values below 20 µg/m³ and individual VOC levels below 0.5 µg/m³. Chamber differential pressure was continuously monitored to maintain a slight positive pressurization (approximately 10 Pa) throughout each test. Tests 5a,b,c and d were conducted simultaneously in these four chambers, as were Tests 6a, 6b, 7a, and 7b, to prevent any impact of sample age or storage conditions from affecting the specimen variability results.

Table 2. Dimensions of test specimens.

Specimen Cod	Length, mm	Width, mm	Thickness, mr	Volume, cm ³	Weight, g	Density, g/cm
OSB1	212.0	112.0	12.5	296.8	167.3	0.564
OSB2	212.0	112.0	11.1	263.6	178.8	0.678
OSB3	212.0	112.0	15.5	368.0	219.4	0.596
OSB4	212.8	113.0	14.8	355.9	226.6	0.637
OSB5a	209.7	112.3	14.2	334.4	199.3	0.596
OSB5b	209.9	112.0	14.0	328.5	203.9	0.621
OSB5c	209.7	110.7	14.3	331.2	194.4	0.587
OSB5d	210.1	111.2	14.5	339.2	195.8	0.577
OSB6a	210.0	112.3	14.4	339.6	202.6	0.597
OSB6b	209.9	112.4	14.3	338.1	196.1	0.580
OSB7a	209.9	111.7	14.7	343.9	203.9	0.593
OSB7b	210.3	112.4	14.8	349.2	207.6	0.595

VOC Sampling and Analysis

A detailed description of the analytical methodology used in this study has been previously reported.²⁰ A summary of the methods is given below.

Chemical Analysis

VOCs from the chamber tests of the OSB specimens were monitored by two separate methodologies: GC/MS and HPLC.

GC/MS Analysis

Sample collection and analysis: Air samples were collected from the dynamic chamber on multilayer Carbotrap 300 tubes, and subsequently desorbed on a Perkin-Elmer ATD400 thermodesorber and analyzed by a Gas Chromatography/Mass Spectroscopy. DB-5 60 m capillary columns (0.25µm film thickness, 0.32 mm ID) were used for separation of VOCs. For tests 1, 2, 3, an HP 5989 MS Engine was used; desorption temperature was 320°C; GC oven

temperature program was from 100°C to 250°C. Tests 4, 5, 6, and 7 were analyzed by an Agilent Technologies MSD 5973; desorption temperature was 350°C; and GC oven temperature program was from -20 to 280°C. For all tests, a three-point calibration using a standard mixture, which included toluene, was performed each time samples were analyzed.

GC/MS qualitative analysis: Identification of emitted compounds from all tests was done for samples taken after 24 h from the beginning of each test. Individual VOCs were identified by comparison of the peak's MS spectrum with the NIST98 library coupled with ChemStation software. Peak retention times, published data and previous analytical experience helped to validate the identification. In some cases, full identification was not possible.

GC/MS quantitative analysis: Two levels of quantification were performed.

Relative concentrations of identified VOCs were determined as the percentage of individual peak counts vs. the total peaks counts. These results should be viewed as *semi-quantitative* only. In many cases, co-elution of peaks resulted in significant integration error.

For ten selected VOCs and TVOC, a more precise quantification was performed. *Heptanal*, *hexanal* and *α-pinene* concentrations were calculated using their extracted ion response factors. The toluene response factor was used for *pentanal*; *formic acid*, *pentyl ester*; *2-heptanone*; *furan*, *2-pentyl*; *2-octenal*; *acetic acid*; and *hexanoic acid*. TVOC was also quantified using the toluene response factor, but with a separately conducted integration of all peaks together.

HPLC Analysis

For determination of aldehydes and carbonyl compounds, samples from the chamber exhaust air were collected on DNPH-treated SPE cartridges (Waters SepPak XPoSure Aldehyde), extracted with acetonitrile and analyzed by HPLC (Varian 9012 Solvent Delivery System / 9050 Variable Wavelength UV-VIS Detector (at 360nm) / Prostar 410 Autosampler. Two Supelcosil LC-18 columns (25cm x 4.6mm, 5 μm) in series at 30°C were used to run a gradient of acetonitrile in water from 60% to 100%. Identification and quantification of target compounds was performed via injection of pure individual standards and calibration of the system using TO-11/IP-6A Aldehyde/Ketone reference standards (Supelco). HPLC analysis was performed for test 4-7.

Data Analysis/Modeling:

Previous work demonstrated that a power law model best describes the emission of VOCs from dry building materials.^{21,22,23,24} Regression analysis was therefore performed to determine a power law fit of the concentration vs. time data (elapsed time ≥ 24 h) for each compound/test according to the equation:

$$C_t = a_c t^b \quad (1)$$

where:

- C_t = chamber concentration of VOC (or TVOC) at time t, mg/m³
- a_c = empirical constant
- b = empirical constant

Standard error values (R^2) for each curve were calculated as indicators of agreement with the power law behavior, and also of analytical variability.

Several methods are possible for calculating VOC emission factors¹⁰, but for dry materials, where concentration change over time is relatively small, the emission factor at time t can be directly calculated from concentration data²⁴ using the following equation:

$$E_t = C_t N/L \quad (2)$$

where:

$$\begin{aligned} E_t &= \text{emission factor at time } t, \text{ mg/m}^2\text{h} \\ N &= \text{chamber air change rate per hour, h}^{-1} \\ L &= \text{product loading ratio (exposed surface area / chamber volume), m}^2\text{/m}^3 \end{aligned}$$

Plotting the values of E_t vs. t and using non-linear regression to fit a power law function to the data yields the following general expression for the power law decay model:

$$E_t = a t^{-k} \quad (3)$$

where:

$$\begin{aligned} a &= \text{empirical constant} \\ k &= \text{decay constant, dimensionless} \end{aligned}$$

Comparison of equation 1, 2, and 3 shows that $a = a_c (N/L)$; and $k = -b$. Thus, for these conditions, the power law decay coefficients can also be calculated directly from the concentration vs. time power law fit.

Experimental Uncertainty Analysis

In order to be able to evaluate emission variability on a specimen by specimen basis, it was first necessary to estimate the uncertainty in the measured VOC concentrations due either to sampling techniques and quantification (GC/MS or HPLC), or due to experimental uncertainties related to control of the chamber environmental conditions. These uncertainty determinations are discussed below.

GC/MS Measurements

The emission factor from a dynamic material emission chamber test with a steady state can be calculated based on Eq. (4):

$$E = \frac{Q}{A} C = \frac{Q}{A} \frac{M}{V_s} = \frac{Q}{A} \frac{1}{V_s} \frac{A_c}{RF_{91} R_{ct}} \quad (4)$$

where E is emission factor ($\text{mg/m}^2\text{/h}$); Q is the chamber flow rate ($\text{m}^3\text{/h}$); A is the surface area of a specimen (m^2); C is the chamber air concentration ($\mu\text{g/m}^3$); M is the mass in the air sample collected in a sorbent tube (μg); V_s is the sampling volume (m^3). A_c is the area under the curve of a selected ion of a compound of interest (area); RF_{91} is the response factor of the ion with a mass-to-charge ratio of 91 of toluene ($\text{area}/\mu\text{g}$); R_{ct} is the relative response factor, which is the

ratio of the response factor of a selected ion of a chemical of interest against that of the ion with the mass-to-charge ratio of 91 of toluene.

The variance of E can be expressed in terms of the variances of the quantities calculated from experimental data associated with each term on the right side of Eq. (4):

$$\sigma_E^2 = \left(\frac{\partial E}{\partial Q}\right)^2 \sigma_Q^2 + \left(\frac{\partial E}{\partial A}\right)^2 \sigma_A^2 + \left(\frac{\partial E}{\partial V_s}\right)^2 \sigma_{V_s}^2 + \left(\frac{\partial E}{\partial A_c}\right)^2 \sigma_{A_c}^2 + \left(\frac{\partial E}{\partial RF_t}\right)^2 \sigma_{RF_t}^2 + \left(\frac{\partial E}{\partial R_{ct}}\right)^2 \sigma_{R_{ct}}^2 \quad (5)$$

where σ_E^2 is the variance of E (mg/m²h), σ_A^2 is the variance of A (m²); $\sigma_{V_s}^2$ is the variance of V_s (m³); $\sigma_{A_c}^2$ is the variance of A_c (m²); $\sigma_{RF_t}^2$ is the variance of RF_t; $\sigma_{R_{ct}}^2$ is the variance of R_{ct} (1/mg);

In general, the uncertainty of A and V_s is considered insignificant, i.e., $\sigma_A \approx 0$ and $\sigma_{V_s} \approx 0$. Therefore, the uncertainty (U) associated with E can be simplified as:

$$U = \sigma_E = \sqrt{\left(\frac{E}{Q}\right)^2 \sigma_Q^2 + \left(\frac{E}{A_c}\right)^2 \sigma_{A_c}^2 + \left(\frac{E}{RF_t}\right)^2 \sigma_{RF_t}^2 + \left(\frac{E}{R_{ct}}\right)^2 \sigma_{R_{ct}}^2} \quad (6)$$

The relative uncertainty (U_r) with the unit of % can be expressed as:

$$U_r = 100 \frac{\sigma_E}{E} = 100 \sqrt{\left(\frac{\sigma_Q}{Q}\right)^2 + \left(\frac{\sigma_{A_c}}{A_c}\right)^2 + \left(\frac{\sigma_{RF_t}}{RF_t}\right)^2 + \left(\frac{\sigma_{R_{ct}}}{R_{ct}}\right)^2} \quad (7)$$

According to the measurements, $\frac{\sigma_Q}{Q} \approx 0.1\%$, $\frac{\sigma_{A_c}}{A_c} \approx 1\%$, and $\frac{\sigma_{RF_t}}{RF_t} \approx 10\%$.

The term σ_Q was calculated from the flow rate data recorded during a chamber test. The term σ_{A_c} was obtained from 20 trials of manual integration of a chromatograph peak. The term σ_{RF_t} was determined from three sets of three-points calibration curves run for a set of chamber test. The term, $\sigma_{R_{ct}}$, was obtained from standard calibrations run over a period of one year.

Uncertainty Analysis for HPLC Measurements

The emission factor from a dynamic material emission chamber test with a steady state can be calculated based on Eq. (8) for the HPLC analysis.

$$E = \frac{Q}{A} C = \frac{Q}{A} \frac{M}{V_s} = \frac{Q}{A} \frac{1}{V_s} \frac{A_c}{RF_c} \quad (8)$$

where RF_c is the response factor of the chemical of interest. The response factor for each compound was obtained from an external calibration with five concentration levels.

With the same procedure for the uncertainty analysis for GC/MS measurements, the relative uncertainty for HPLC measurements can be expressed as:

$$U_r = 100 \frac{\sigma_E}{E} = 100 \sqrt{\left(\frac{\sigma_Q}{Q}\right)^2 + \left(\frac{\sigma_{A_c}}{A_c}\right)^2 + \left(\frac{\sigma_{RF_c}}{RF_c}\right)^2} \quad (9)$$

The uncertainties from chamber flow rates and the area counts under a chromatograph are the

same for the GC/MS analysis, i.e., $\frac{\sigma_Q}{Q} \approx 1\text{E}^{-3}$ and $\frac{\sigma_{A_c}}{A_c} \approx 1\text{E}^{-2}$. The standard deviation of the response factors from five-point calibration curves obtained at three different dates was used as the uncertainty from the response factor.

Uncertainty in Chamber Environmental Control

As previously described, the four chambers used in this study were carefully matched (dimensions, materials of construction) as were the four sample holders. For each chamber system, temperature, relative humidity of the exhaust air, chamber pressure, and inlet flow rate were continuously monitored and % standard deviations calculated.

RESULTS AND DISCUSSION

Before discussing specimen variability, the confounding issue of analytical uncertainty will first be addressed. Variability analysis will proceed from qualitative to quantitative.

Experimental Analytical Uncertainty

Uncertainty in Chamber Operation Conditions

Supply airflow rate, chamber temperature, and exhaust air humidity were carefully controlled and continuously monitored for all tests. The mean and % standard deviations of these parameters observed for tests OSB5a, b, c, and d are summarized in Table 3. The highest observed environmental uncertainty was in the control of relative humidity with a relative standard deviation of 4%, equal to a deviation of only 2% RH units from the target value.

Table 3: Chamber environmental conditions.

Test Code	Air Flow, mL/min		Chamber Temp, °C		Relative Humidity, %	
	mean	SD, %	mean	SD, %	mean	SD, %
OSB 5a	830.6	0.04	22.97	1.45	48.1	3.26
OSB 5b	830.6	0.02	22.97	1.45	48.1	2.80
OSB 5c	833.1	0.34	22.97	1.45	50.0	4.02
OSB 5d	836.3	0.04	22.97	1.45	51.6	0.55

Uncertainty analysis for GC/MS measurements

Table 4 provides the calculated relative uncertainty (U_r) for several routinely calibrated VOCs. The uncertainty from the relative response factor (R_{ct}) dominates the overall uncertainty caused by experimental error including analytical error with GC/MS. The uncertainty level is compound-specific, ranging from ~ 13 to 35%.

Table 4. Relative uncertainty for several target compounds analyzed by GC/MS.

Class	Compound	$\frac{\sigma_{R_{ct}}}{R_{ct}}$ (%)	U _r (%)	Class	Compound	$\frac{\sigma_{R_{ct}}}{R_{ct}}$ (%)	U _r (%)
Aliphatics	Hexane	15.38	18.38	Aromatics	Benzene	14.81	17.90
	Heptane	7.89	12.78		Benzene, 1,4-dimethyl	10.42	14.47
	Octane	16.35	19.19		Benzene, 1,2-dimethyl	17.89	20.52
	Nonane	19.23	21.70		Ethyl benzene	11.21	15.05
	Undecane	16.00	18.89		Styrene	8.86	13.40
	Dodecane	13.98	17.22		Naphthalene	9.32	13.70
	Tetradecane	20.00	22.38		Benzene, 1,2,4-trimethyl	22.00	24.19
Aldehydes	Butanal	17.65	20.31	Terpenes	α -Pinene	33.33	34.82
	Pentanal	16.67	19.46		Camphene	19.23	21.70
	Hexanal	20.00	22.38		3-Carene	15.22	18.24
	Heptanal	14.29	17.47		Limonene	16.67	19.46
	Nonanal	18.18	20.77				
	Decanal	19.05	21.54				

Uncertainty analysis for HPLC measurements

Table 5 summarizes the overall uncertainty associated with emission factors of compounds analyzed by HPLC. The uncertainty from the individual response factor (RF_c) dominates the uncertainty associated with experimental error with HPLC. In contrast to GC/MS analysis, which attempts to identify (and quantify) as broad a range of compounds as possible, the HPLC analysis performed here targets carbonyl compounds only. This analytical focus is reflected in the relative improvement of the calculated uncertainties (ranging from about 2.5 to 5%) and highlights the importance of proper selection of analytical methods for the quantification of VOC emissions.

Table 5. Relative uncertainty for compounds analyzed by HPLC.

Compound	$\frac{\sigma_{RF_c}}{RF_c}$ (%)	U _r (%)	Compound	$\frac{\sigma_{RF_c}}{RF_c}$ (%)	U _r (%)
Acetaldehyde	4.56	4.67	Hexanal	2.74	2.91
Acetone	4.07	4.19	Propanal	4.40	4.51
Acrolein	4.69	4.79	m-Tolualdehyde	4.19	4.30
Benzaldehyde	3.51	3.65	o-Tolualdehyde	4.58	4.69
Benzaldehyde, 2,5-dimethyl	2.34	2.54	p-Tolualdehyde	4.79	4.89
Butanal	3.60	3.73	Pentanal	4.87	4.97
Crotonaldehyde	4.04	4.17	iso-Pentanal	4.71	4.81
Formaldehyde	4.33	4.44			

Emission Variability: Qualitative Analysis (GC/MS)

The results of the qualitative determination of all identifiable VOCs in the 24hr chamber samples are summarized by compound class in Table 6. Table 7 gives the complete analysis by individual compounds. In general, the OSB specimens exhibited similarities in terms of the type of compounds emitted. Aldehydes, organic acids, 2-pentyl furan and α -pinene dominated the emission profiles. There are, however, some clear distinctions that can be made between the specimens based on this qualitative data.

Table 6. Summary of approximate VOC distributions (% of TVOC) at 24 hours by GC/MS.

VOC Class	OSB 1	OSB 2	OSB 3	OSB 4	OSB 5a	OSB 5b	OSB 5c	OSB 5d	OSB6 a	OSB 6b	OSB 7a	OSB 7b
Aldehydes	39.37	33.98	74.08	13.76	30.04	25.29	19.09	31.34	20.98	14.07	29.79	21.47
Ketones		3.75		5.59	3.59	8.19	6.25	5.93	8.23	9.37	9.72	3.70
Acids	0.34	7.67	4.20	11.44	6.71	18.78	24.61	6.99	25.41	16.73	24.56	22.07
Alcohols	3.82	5.68	0.23	4.00	2.59	0.81	3.22	5.69	5.71	3.65	4.99	3.25
Esters	1.43	0.66		0.93	1.12	3.05	2.33	2.84	1.90	1.27	2.88	2.85
Furans	2.78	16.84	4.60	10.41	6.32	9.04	8.46	8.17	9.82	9.30	10.76	6.78
Non-Aromatic Hydrocarbons	33.77	3.46	2.31	8.26	5.10	5.41	4.46	5.62	2.75	4.95	1.47	9.18
Aromatic Hydrocarbons	2.28		0.73	4.32		1.25	0.83	1.10	2.05	3.52	0.59	7.11
Chlorinated Hydrocarbons	0.78			1.80			1.18	0.49	0.14	7.74	0.20	5.04
Terpines	3.40	1.33	3.40	0.54	1.61	2.30	0.86	1.27	0.38	0.46	0.49	0.98
Total Identified VOCs (%):	87.96	73.36	89.56	61.06	57.09	74.10	71.29	69.44	77.38	71.04	85.43	82.42

Mill-mill variability is evident from review of the data from tests OSB1, 2, and 3. Non-aromatic hydrocarbons dominate OSB1 emission (many of these VOCs were *only* found with this specimen). In contrast, the 2-pentyl furan content of OSB2 is relatively high, while aldehydes (particularly hexanal) dominate the emission from OSB3. OSB3 also exhibited a much broader range of furans than was observed with the other specimens. Ketones were not detected from OSB1 or OSB3, but were emitted in significant quantities from the remaining specimens (all from Mill B). The absence of detected hexanoic acid for tests 1, 2, and 3 may be due more to the switch to higher desorption and column temperatures in the later tests than to any compositional changes in the OSB specimens. The chlorinated hydrocarbon 1,4-dichloro benzene was detected in specimen OSB1 but not in OSB2 or 3. This compound showed interesting behavior in that significant quantities were detected in the emissions from specimens 6b and 7b, and lesser amounts from 5c, while the matched specimens for each of these tests (6a, 7a, and 5a,b,d) showed little or no emission of this VOC. Chamber background checks conducted prior to testing did not show the presence of this compound. Three separate chamber systems were used in tests 5c, 6b and 7a. It appears that this chemical in particular shows a high degree of variability in emission level on a specimen-by-specimen basis even from the same test panel. Significant specimen-specimen variability was also observed in alcohol and organic acid emissions in Tests 5a-d; and in hydrocarbon emission (both aromatic and non-aromatic) for tests 7a and 7b.

Table 7. Summary of approximate VOC concentrations (% of TVOC) at 24 hours by GC/MS.

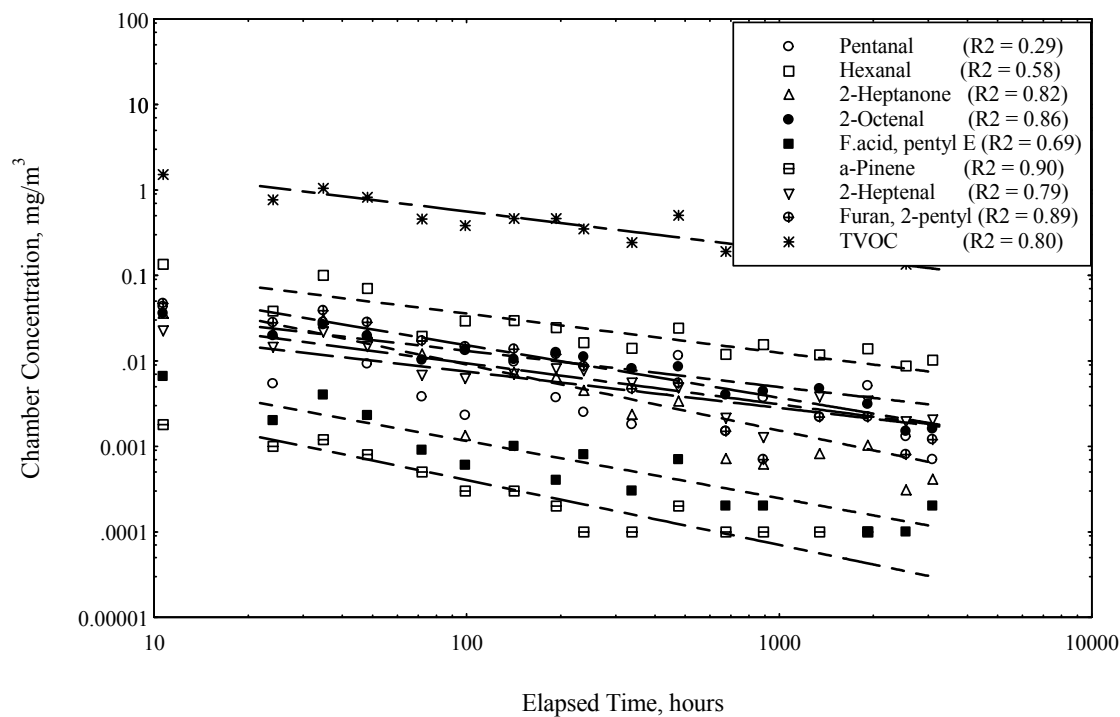
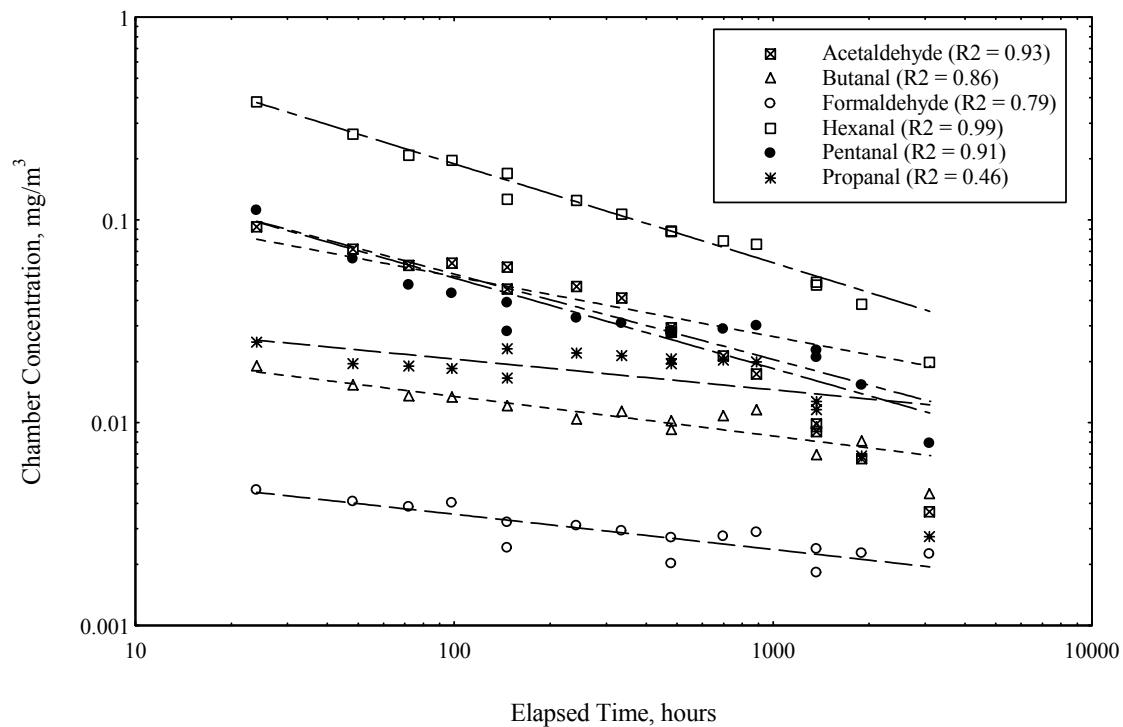
CLASS	VOC	OSB 1	OSB 2	OSB 3	OSB 4	OSB 5a	OSB 5b	OSB 5c	OSB 5d	OSB 6a	OSB 6b	OSB 7a	OSB 7b
Aldehydes	2,4-Decadienal		1.73		0.43		0.39	0.51	0.63	0.26	0.20	0.23	0.30
	2-Heptenal		2.91	0.57	0.94	1.15	1.38		0.97	2.85	2.33	3.97	1.11
	2-Octenal	11.40	2.28	1.28	1.85	2.51	2.02	4.76	3.59	3.63	3.24	4.17	2.89
	Benzaldehyde	0.35	0.57				0.53		0.39	0.48	0.84		1.00
	Benzaldehyde, 2-hydroxy-		1.61										
	Benzaldehyde, 3-methyl-						1.49		0.57	0.33	0.43		1.32
	Butanal	0.76		0.97	0.50	1.33	1.69	1.07	1.87			0.38	1.59
	Decanal	0.56	3.83	0.31	0.76			0.15	0.18				0.13
	Furfural	0.37	1.26										
	Heptanal	1.60	2.68	1.03	0.38	0.26	0.40	0.20	0.26	0.38	0.34	0.46	
	Hexanal	19.23	11.82	65.12	4.81	17.18	11.92	9.58	19.38	10.59	5.57	17.61	9.62
	Nonanal	1.72	5.30	0.30	0.84			0.65	0.40	0.23	0.17	0.22	0.42
Ketones	Pentanal	3.38		4.50	3.25	7.61	5.47	2.17	3.11	2.22	0.96	2.76	3.09
	1-Hepten-3-one		1.69		0.83	0.61		1.14	0.78	1.22	1.25	2.05	0.45
	2,11-Dodecanedione				0.88	1.87	0.99	0.82	1.23	0.62	0.54	0.46	0.59
	2-Heptanone		2.07		2.84	1.11	6.42	1.76	1.75	3.78	4.75	3.80	0.96
	2-Heptanone, 6-methyl-									0.21	0.36	0.18	
	3-Nonen-2-one				0.27			0.43	0.39	0.30	0.22	0.22	0.20
	3-Octanone							1.21	0.72	1.57	1.92	2.59	1.04
	3-Octen-2-one												
Acids	5-Decanone				0.35		0.38	0.37	0.43	0.27	0.14	0.19	0.15
	6-Undecanone				0.43		0.39	0.51	0.63	0.26	0.20	0.23	0.30
Alcohols	Acetic acid	0.34	7.67	4.20	4.24	2.52	6.75	6.26	1.53	11.07	7.36	12.62	10.55
	Hexanoic acid				7.20	4.19	12.03	18.35	5.47	14.34	9.36	11.94	11.52
Alcohols	1-Butanol	1.11											
	1-Butanol, 2-methyl-, acetate	0.88	0.52										
	1-Hexanol											0.23	0.24
	1-Hexanol, 2-ethyl-				1.07		0.81	0.98		0.48	0.43	0.31	0.80
	3,5-Octadien-2-ol				0.93	0.66		1.00	1.42	1.21	0.95	1.36	1.14
	3-Octen-2-ol		2.28		1.55	1.93			3.36	2.56	1.74	2.75	1.07
	Octanal	1.06	2.87	0.23	0.45			1.23	0.92	1.47	0.53	0.34	
Esters	Phenol	0.76											
	Acetic acid, 2-EEE	0.88											
	Acetic acid, methyl ester											0.29	0.22
	Acetic acid, pentyl ester	0.55	0.66				0.38	0.08	0.11	0.27	0.25	0.23	
	Formic acid, pentyl ester				0.22	0.69	1.26	1.12	1.14	0.63	0.46	1.86	0.81
	Hexanoic acid, methyl ester									0.22	0.22	0.21	
	Hexanoic acid, pentyl ester				0.43	0.43	0.86	0.65	0.76	0.59	0.24	0.29	1.17
Furans	Pentanoic acid, pentyl ester				0.29		0.54	0.49	0.83	0.20	0.10		0.65
	Furan 2-methyl			0.32									
	Furan, 2-ethyl-			0.59									
	Furan, 2-n-butyl		1.02	0.68									
	Furan, 2-pentyl-	2.78	15.83	3.01	10.41	6.32	9.04	8.46	8.17	9.82	9.30	10.76	6.78

Table 7 (continued). Summary of approx. VOC concentrations (% of TVOC) at 24h by GC/MS.

CLASS	VOC	OSB 1	OSB 2	OSB 3	OSB 4	OSB 5a	OSB 5b	OSB 5c	OSB 5d	OSB 6a	OSB 6b	OSB 7a	OSB 7b
Non-Aromatic Hydrocarbons	1-Heptene			0.22			0.81	0.67	0.38	0.12	0.16	0.21	0.36
	1-Hexene			0.40									
	1-Pentene				0.35	0.71	0.56	0.49	0.71	0.08	0.48		0.26
	C10H22	1.74											
	C11H24	2.38											
	C12H26	0.34											
	C9H20	0.91											
	Cyclopentane, methyl-	0.68											
	Decane	0.61	0.68	0.24	1.46	0.53	1.14	0.97	0.76	1.46	2.69	0.43	5.70
	Decane, 2,6-dimethyl	0.85											
	Dodecane	0.45	0.87	0.31									
	Heptane, 2,4-dimethyl-	3.74											
	Heptane, 2-methyl-	0.96											
	Heptane, 4-ethyl-	0.85											
	Hexane	1.07		0.59									
	Nonane				2.45	0.58	1.41	0.54	0.30	0.43	0.74	0.39	0.38
	Nonane, 2,6-dimethyl-	1.28											
	Nonane, 2-methyl-	0.56											
	Octane, 4-methyl-	0.56											
	Octane, 4-methyl-	2.52											
	Pentadecane				0.82					0.14			
	Pentane	12.5	1.02		1.08	3.28	1.50	1.19	2.82	0.26	0.53	0.23	1.37
	Pentane, 2-methyl-	1.78											
	Tetradecane				1.51								
	Undecane		0.88	0.55	0.58			0.61	0.66	0.25	0.35	0.20	1.11
Aromatic Hydrocarbons	Benzene	0.74		0.42	0.27		0.39	0.43	0.40	0.06	0.26		0.61
	Benzene, 1,3,5-trimethyl-									0.94	1.44	0.39	2.55
	Benzene, 1,3-dimethyl-	0.78			2.70		0.42	0.11	0.25	0.44	0.12	0.20	0.61
	Benzene, 1-ethyl-3-methyl-									0.46	0.72		1.12
	Benzene, 1-methyl-3-(1-ME)			0.31									0.38
	Benzene, propyl-												1.84
Cl-HCs	Toluene	0.76			1.34		0.43	0.29	0.44	0.14	0.99		
	Benzene, 1,4-dichloro-	0.78			1.80			1.18	0.49	0.14	7.74	0.20	5.04
Terpines	3-Carene			0.39									
	α -Pinene	2.33	1.33	1.70	0.54	1.61	2.30	0.86	1.27	0.38	0.46	0.49	0.98
	β -Pinene			0.92									
	Limonene	1.07		0.39									

Emission Variability: Quantitative Analysis

Examples of VOC chamber concentration data are given in Figure 1 (results from GC/MS samples) and Figure 2 (from HPLC analyses). The curves shown in these figures are the power law functions fitted to the experimental data. Correlation coefficients calculated for each VOC are indicated in the figure legends. The analytical variability as expressed by the correlation coefficients of the fitted curves was fairly typical in the example shown. VOCs quantified via GC/MS showed R^2 values ranging from 0.29 (pentanal) to 0.90 for α -pinene. As described earlier, similar R^2 values for HPLC analysis improved to between 0.46 (propanal) and 0.99 (hexanal). HPLC is obviously the method of choice for compounds such as hexanal and pentanal.

Figure 1: VOC concentration observations: Test OSB 6b (GC/MS data).**Figure 2: VOC concentration observations: Test OSB 6b (HPLC data).**

Examples of the modeled emission factors vs. time for hexanal (via HPLC) for tests 4 through 7 are shown in Figure 3 (the curve symbols in this plot are merely provided to assist with identification and do not represent data points). Note the broad range of calculated emission factors for this single compound from the OSB specimens tested.

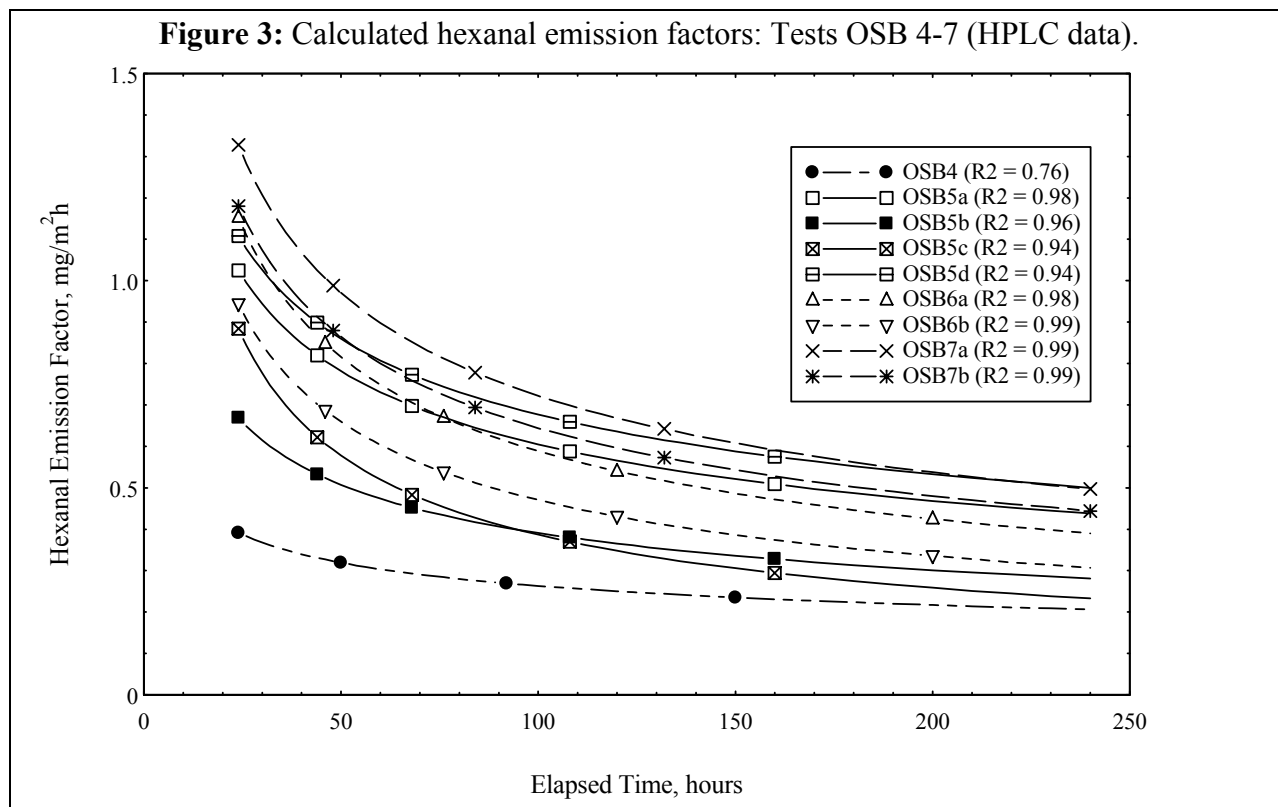


Table 8 summarizes the quantitative uncertainty analysis presented here. The test results are grouped vertically by the comparison made. For example, the first row in the table looks at mill-mill variability as revealed from tests OSB 1, 2 and 3. For each group of tests, representative VOCs were picked with relatively high R^2 values from the concentration vs. time power fits. No point looking for specimen variability with noisy analytical data – this reflects the reality that not all compounds can be reliably quantified with the particular combination of sample tube, desorption apparatus, GC column and operating conditions selected to give broad detection capabilities. For each VOC, the emission factor was calculated at 120 hours for each of the test specimens involved. For example, pentanal emission factors calculated for OSB 1, 2 and 3 had a mean value of 0.148 mg/m²h with a relative standard deviation of 135%. With an analytical uncertainty of approximately 20%, the pentanal emission variability at 120 hours thus exceeded the analytical uncertainty by a factor of about 7 to 1.

Table 8: Summary of VOC Emissions Variability.

Comparison Type	Analytical Method	Modeled VOC	U _r , %	Mean R ²	E ₁₂₀ , mg/m ² h				SD % / U _r %
					Min	Max	Mean	SD %	
Case 1: Different OSB Manufacturer (3 Mills) (OSB 1,2,3)	GC/MS	α-Pinene	35	0.68	0.0034	0.0157	0.0075	94	2.7
		Furan, 2-Pentyl		0.84	0.0069	0.0690	0.0454	74	
		Hexanal	22	0.81	0.0667	1.3267	0.5177	136	6.1
		Pentanal	20	0.83	0.0287	0.3787	0.1481	135	6.9
Case 2: Different Production Dates, Same Mill (OSB 4,5b,7b)	GC/MS	α -Pinene	35	0.80	0.0001	0.0038	0.0016	121	3.5
		Formic acid, PE		0.85	0.0004	0.0030	0.0018	73	
		Furan, 2-Pentyl		0.77	0.0116	0.0220	0.0181	31	
	HPLC	Butanal	4	0.77	0.0180	0.0366	0.0266	35	9.5
		Hexanal	3	0.90	0.2502	0.5964	0.4039	44	15.1
		Pentanal	5	0.94	0.0740	0.1582	0.1142	37	7.4
Case 3: Different Boards (2) from Same Mill, Same Production Dates (OSB 6a,b,7a,b)	GC/MS	2-Heptenal		0.73	0.0159	0.0218	0.0189	16	
		2-Octenal		0.74	0.0268	0.0302	0.0283	6	
		α -Pinene	35	0.90	0.0008	0.0009	0.0008	4	0.1
		Formic acid, PE		0.85	0.0014	0.0026	0.0020	24	
		Furan, 2-Pentyl		0.84	0.0220	0.0358	0.0290	24	
		Hexanal	22	0.73	0.0820	0.1139	0.0985	15	0.7
		TVOC		0.75	0.4464	1.2878	0.8281	47	
	HPLC	Acetaldehyde	5	0.95	0.1247	0.1520	0.1397	9	1.8
		Butanal	4	0.90	0.0324	0.0366	0.0339	6	1.6
		Formaldehyde	4	0.91	0.0085	0.0096	0.0092	5	1.2
		Hexanal	3	0.99	0.4305	0.6684	0.5589	18	6.2
		Pentanal	5	0.96	0.1187	0.1582	0.1396	14	2.8
Case 4: Different Locations within the Same Board (OSB 5a,b,c,d)	GC/MS	α -Pinene	35	0.60	0.0013	0.0038	0.0021	53	1.5
		Formic acid, PE		0.62	0.0015	0.0030	0.0020	36	
		Furan, 2-Pentyl		0.67	0.0114	0.0207	0.0154	26	
		TVOC		0.50	0.2481	0.4646	0.3384	29	
	HPLC	Acetaldehyde	5	0.90	0.1497	0.2247	0.1861	17	3.7
		Butanal	4	0.75	0.0254	0.0400	0.0310	21	5.6
		Formaldehyde	4	0.76	0.0168	0.0254	0.0208	19	4.2
		Hexanal	3	0.95	0.3478	0.6355	0.4785	30	10.4
		Pentanal	5	0.97	0.1105	0.1874	0.1414	27	5.4

Using the same comparative approach, Table 8 indicates a slightly higher degree of variability for Case 2 (same mill, different production dates): the ratio of uncertainties (SD %/ U_r %) for α-pinene equals 3.5 vs. 2.7 for Case1. While formaldehyde emission from boards produced on the same date by the same mill (Case 3) was relatively consistent, hexanal and pentanal emission showed a greater degree of variability (HPLC data). This trend was not observed with the

GC/MS data for hexanal, however, likely due to its higher analytical uncertainty for this compound. In Case 4 (multiple samples from the same board), hexanal emission exhibited even higher variability.

CONCLUSIONS

A series of tests of OSB were conducted to examine the degree of variability that can occur in the emissions of VOCs from a single building product. While the sample size is small, and limits detailed statistical analysis, some observations of interest were found.

Experimental uncertainty with the GC/MS was found to be strongly compound-specific, with a mean value of about 19% (ranging from ~12% to ~35%). HPLC uncertainty, for a much narrower spectrum of VOCs, and a system optimized for their collection and analysis, was not surprisingly much lower at about 4.2 % (2.5 to 5% range).

In the analysis of OSB emissions variability, mill-mill differences were evident (qualitatively and quantitatively), as were differences between production dates, between individual panels with the same production date, and even between specimens taken from a single panel.

In summary, variability inherent within the building material itself should be considered when comparing different building material options (as in labeling schemes) or in the development and validation through chamber testing of models for VOC emission. Variability assessment should be conducted while keeping in mind appropriate selection of target VOCs and analytical methods so as to minimize analytical error that could otherwise mask variability. Round robin certification of test labs should consider these factors and design their comparisons accordingly. Precise definition and control of emission testing protocols is essential, but not the complete answer to emissions standardization.

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Key Words

- material emissions
- oriented strand board
- chamber testing
- VOC
- Volatile organic compounds
- Variability
- Uncertainty