



# VOCs Emissions from Multiple Wood Pellet Types and Concentrations in Indoor Air

Lydia Soto-Garcia,<sup>†</sup> William J. Ashley,<sup>‡</sup> Sandar Bregg,<sup>‡</sup> Drew Walier,<sup>‡</sup> Ryan LeBouf,<sup>§</sup> Philip K. Hopke,<sup>\*,†,‡</sup> and Alan Rossner<sup>‡</sup>

<sup>†</sup>Center for Air Resources Engineering and Science, Clarkson University, Potsdam, New York 13699, United States

<sup>‡</sup>Institute for the Sustainable Environment, Clarkson University, Potsdam, New York 13699, United States

<sup>§</sup>National Institute for Occupational Safety and Health, Morgantown, West Virginia 26505, United States

## S Supporting Information

**ABSTRACT:** Wood pellet storage safety is an important aspect for implementing woody biomass as a renewable energy source. When wood pellets are stored indoors in large quantities (tons) in poorly ventilated spaces in buildings, such as in basements, off-gassing of volatile organic compounds (VOCs) can significantly affect indoor air quality. To determine the emission rates and potential impact of VOC emissions, a series of laboratory and field measurements were conducted using softwood, hardwood, and blended wood pellets manufactured in New York. Evacuated canisters were used to collect air samples from the headspace of drums containing pellets and then in basements and pellet storage areas of homes and small businesses. Multiple peaks were identified during GC/MS and GC/FID analysis, and four primary VOCs were characterized and quantified: methanol, pentane, pentanal, and hexanal. Laboratory results show that total VOCs (TVOCs) concentrations for softwood (SW) were statistically ( $p < 0.02$ ) higher than blended or hardwood (HW) (SW:  $412 \pm 25$ ; blended:  $203 \pm 4$ ; HW:  $99 \pm 8$ , ppb). The emission rate from HW was the fastest, followed by blended and SW, respectively. Emissions rates were found to range from  $10^{-1}$  to  $10^{-5}$  units, depending upon environmental factors. Field measurements resulted in airborne concentrations ranging from  $67 \pm 8$  to  $5000 \pm 3000$  ppb of TVOCs and 12 to 1500 ppb of aldehydes, with higher concentrations found in a basement with a large fabric bag storage unit after fresh pellet delivery and lower concentrations for aged pellets. These results suggest that large fabric bag storage units resulted in a substantial release of VOCs into the building air. Occupants of the buildings tested discussed concerns about odor and sensory irritation when new pellets were delivered. The sensory response was likely due to the aldehydes.

## INTRODUCTION

Interest in wood as a building heating fuel is expanding in the United States.<sup>1,2</sup> Wood pellets have become a popular choice for biomass due to their ease in transportation, storage, and use. Thus, it is important to understand their potential health impacts to building occupants. While immediate health concern with wood pellet storage is the off-gassing of carbon monoxide (CO),<sup>3</sup> another concern is the adverse impact of indoor air quality due to the off-gassing of volatile organic compounds (VOCs) from storage of wood pellets.<sup>4–6</sup> VOCs constitute a significant class of indoor air contaminants. A variety of nonindustrial building investigations and indoor air quality studies found that 60% of the VOCs indoors maybe the result of emission from building materials and furnishings.<sup>7–10</sup> The remaining VOCs may arise from activities in the home and/or infiltration of outside air.

VOCs refer to a group of organic chemicals that have a relatively high vapor pressure at room temperature.<sup>11,12</sup> Each chemical has its own potential for causing different health effects including short-term effects (eye, nose and throat irritation, headaches, nausea/vomiting, dizziness, worsening of asthma symptoms) and long-term terms effect (cancer, liver damage, kidney damage, central nervous system damage).<sup>13,14</sup> Even low concentration exposures can result in health effects such as irritation to the eyes and mucous membranes.<sup>15</sup>

**Background.** The bulk storage of wood pellets in confined spaces produce various gases including carbon monoxide (CO),

carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and a variety of volatile organic carbons (VOCs) including hexanal and monoterpenes that accumulate in the air and can reach to concentrations that result in discomfort and may be a health hazard.<sup>3,16–20</sup>

Svedberg and Galle<sup>4</sup> investigated complaints of eye irritation and odor in a pellet factory in Sweden. They identified the presence of hexanal, pentanal, methanol, acetone, and carbon monoxide. A subsequent study<sup>5</sup> investigated and described the presence and formation of volatile compounds (VOCs), particularly hexanal and carbon monoxide from the storage of wood pellets. They also monitored the emissions from kiln drying of wood and determine that the emissions were not specific to wood pellet production but were more general in nature. Svedberg et al.<sup>5</sup> concluded that the storage of wood pellets resulted in high levels of hexanal and carbon monoxide. Hexanal concentrations were measured to be  $\sim 320$  to  $365$  mg/m<sup>3</sup> with peak values near the pellet pile in a warehouse. In a domestic, sealed pellet storage room, values of  $70$ – $80$  mg/m<sup>3</sup> were measured 18 h after a fresh pellets delivery. Adjacent to the storage room, hexanal concentrations of  $0.056$  to  $0.084$  mg/m<sup>3</sup> were observed. Carbon monoxide concentrations exceeded the Swedish permissible exposure level of  $40$  mg/m<sup>3</sup> in the

**Received:** June 23, 2015

**Revised:** September 6, 2015

**Published:** September 11, 2015



warehouse and peaked at  $123 \pm 10 \text{ mg/m}^3$  in the domestic storage room 18 h after fresh pellet delivery. Their results showed a high potential for both occupational and residential health hazards.

Arshadi et al.<sup>6</sup> examined the VOC emissions from pellets made of blends of pine and spruce. The fatty and resin acid concentrations were measured using gas chromatography–mass spectrometry (GC/MS) for newly produced pellets and those aged for 2 and 4 weeks. The concentrations of aldehydes and ketones were determined by high performance liquid chromatography (HPLC) at 0, 2, and 4 weeks to explore the relationships between the fatty acid content and the resulting carbonyl emissions. They found a strong correlation between the pine fraction in the pellets and the fatty/resin acid content, but the influence decreased over the storage time. The fatty and resin acid concentrations decreased by 40% during the 4 week storage period. The drying temperature also influenced the aldehyde and ketone emissions of fresh pellets. The amounts of emitted aldehydes and ketones generally decreased by 45% during storage as the fatty/resin acids oxidized. Thus, they concluded that oxidation of the fatty acids was the primary mechanism for the generation of the oxygenated VOCs.<sup>16</sup>

Also, Arshadi and Gref<sup>21</sup> suggested that the amounts and compositions of VOCs emitted from stored pellets were strongly correlated with the drying temperature and quality of the raw material as well as the self-heating of the stored pellets. The major constituents of VOC emitted from wood pellets were found to be the aldehydes. Aldehydes are also known irritants to eyes and mucous membranes. Methanol is also known to be sensitizing. Pentanal and hexanal have been identified as causing unpleasant, irritating odors in confined areas.<sup>22</sup> Hexanal was hypothesized to form through the auto-oxidation of linoleic acids.<sup>20</sup>

The aim of this study was to determine concentration and emission rates of the VOC's from hardwood (HW), softwood (SW), and a blended mixture pellets used in the northeastern United States employing laboratory and field studies. There are additional VOCs emitted by the wood pellets such as terpenes, but for the purpose of this project, the focus was on the VOCs that were products of the degradation of wood pellets during bulk storage.

## ■ EXPERIMENTAL SYSTEM

The laboratory study of stored wood pellets was conducted in similar manner as Soto-García et al.,<sup>23</sup> Kuang et al.,<sup>24</sup> and Fan and Bi.<sup>25</sup> The wood pellets were stored in 20 gallon steel drums (20 in. in height and 16 in. in diameter). Two quick connects were inserted through each lid. The drums were sealed by a metal ring with a gasket to maintain an airtight fit and avoid external reactions process. Measurements from each drum were performed every 24 h for around 30 days. Wood pellet samples were obtained from a local manufacturer. Because of the greater abundance of hardwood in northern New York, more hardwood pellets and blended softwood/hardwood pellets are sold in this area. Therefore, this study included hardwood, softwood and blended pellets (typically ~60% hardwood). Emissions at different temperature conditions (6–8, 22, and 30 °C) were measured only for hardwood pellets. In general, the pellet samples were ~6 mm in diameter and 6–25 mm in length with a bulk density of ~18 kg/m<sup>3</sup> (40 lbs/ft<sup>3</sup>). For more details, refer to Soto-García et al.<sup>3</sup>

VOCs samples were collected in the laboratory studies using 400 mL or 1 L evacuated stainless steel canisters (Entech, Inc., Simi Valley, CA) with a fused silica coating inside the canisters.<sup>26</sup> Each canister was cleaned and evacuated using an automatic canister cleaner (Entech 3100A, Entech, Inc., Simi Valley, CA). Samples were collected every 24 h for the duration of the experiment, approximately 20–30

days depending upon the temperature the drums were stored and when the concentrations plateaued. Using a quick release fitting attached to the canister and a complementary quick release fitting connected to the top of the drum, a headspace sample was collected (grab sample) with an evacuated canister. Immediately after sampling, the canisters were pressured to approximately 1.5 atm.

Field samples were collected from a variety of locations where pellets are stored, but mainly from work places (WP) and homes. The locations included the following: two residential basements (Massena and Lisbon, NY) (Home 1 and 2), Massena Chamber of Commerce (WP/CC), the Wild Center in Tupper Lake (WP/WC), Walker Center (WP/WAC), a field house at Clarkson University (CU) with an enclosed room, and a small storage unit supplying pellets for a 20 kW boiler. Storage capacities ranged from 2 ton to 30 ton of wood pellets and means of storage included fabric bags, a trailer, stacked individual bags, and wood enclosures. Table S2 contains details about the field sampling sites locations.

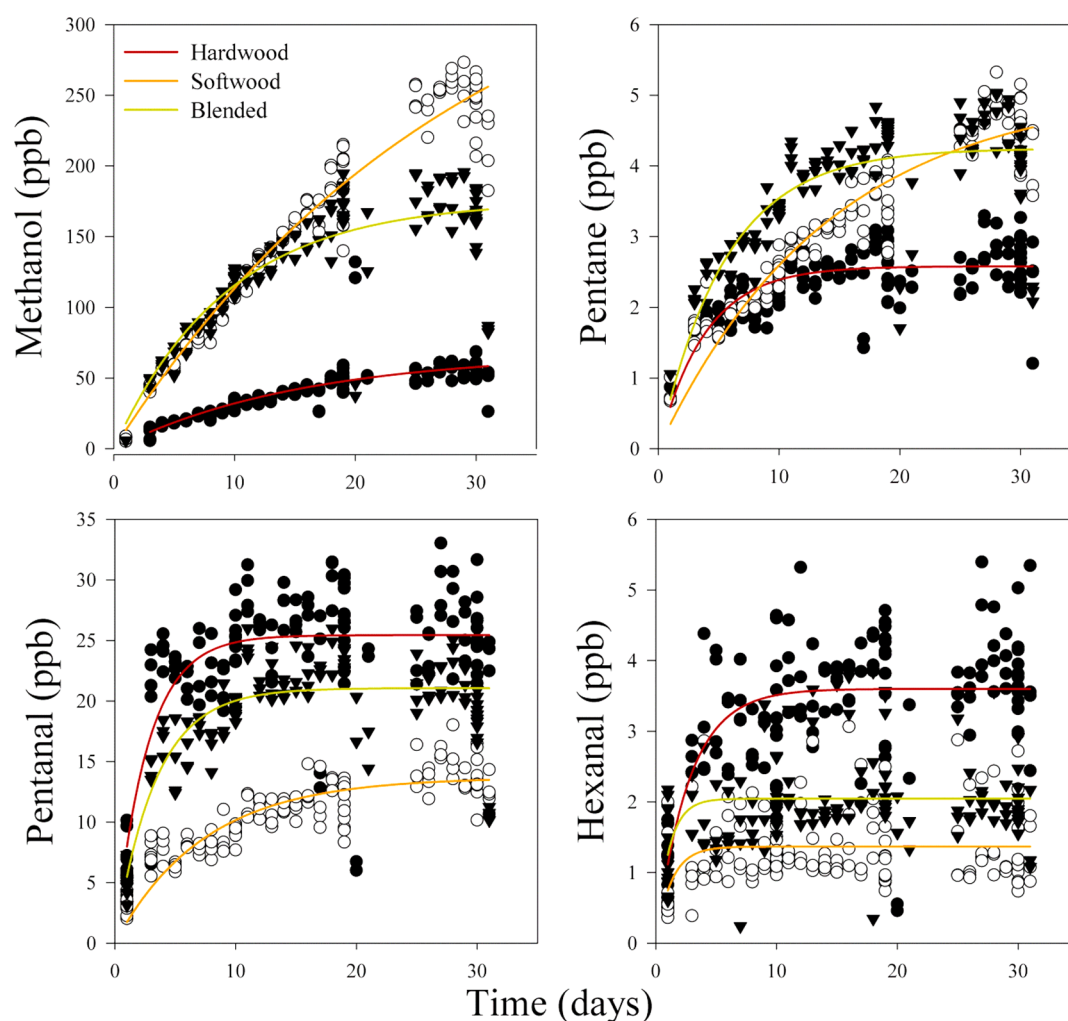
The samples were routinely collected in the room in close proximity (within 1.5 m) from storage bin using 400 mL, 1 L, and 6 L canisters. A total of 69 whole air samples were collected at 6 locations during the heating season of November 2014 to March 2015. The field sampling was designed to observe the concentrations of VOCs in the room surrounding the storage bin. The data from the drum studies provided information on the emission rates of select VOCs, and the field sampling was designed to evaluate the concentrations of VOCs for new and aged pellets. The samples were collected immediately after delivery of a new batch of pellets and then 4 weeks after the pellets were delivered. Information on temperature at the different sites and ages of the pellets when the samples were collected can be found in Table S2. Temperatures were estimated based on the nature of the bin and its location relative to the structure to which it provides pellet storage. The Walker Center (WC) bin has electric heat that ensures that the pellets do not freeze.

## ■ ANALYSIS

Within 1–3 days of collecting the laboratory samples, the canisters were analyzed using GC FID (Hewlett-Packard 5890 series II) for quantification. A subset of samples were analyzed using GC/MS (Hewlett-Packard 5890 series II with a 5971 mass spectrometer) to characterize and/or identify the major peaks in the pellet samples. Typical chromatograms for soft and hardwood pellets are shown in Figure S1

Field samples were analyzed on a Trace Gas Chromatograph Ultra (Thermo Electron Corp.) with a flame ionization detector (FID) using a 7100A preconcentrator (Entech, Inc., Simi Valley, CA). The sample from the canister was drawn into the preconcentrator from one of the four autosampling inlets. The oven temperature of the GC/FID was initially set for 50 °C and held for 2 min. The temperature increased, ramp 1, to 130 °C at a rate of 5 °C min<sup>-1</sup>. Ramp 2 increased the temperature to 180 °C at a rate of 20 °C min<sup>-1</sup> with the final holding time set at 20 min at 180 °C. Sample duration was 20.70 min. The flame ionization detector (FID) was set to a base temperature of 250 °C. The air, hydrogen, and make up were set to flows of 350, 35, and 30 mL/min, respectively.

The canisters were cleaned with ultrahigh-purity nitrogen as discussed in US EPA Method TO-15.<sup>27</sup> Blank corrections were not made to the measured concentrations in this study because all of the blank concentrations were well below the detection limits. The analytical precision for replicate analyses of the samples and standards was within  $\pm 10\%$ . Five-point calibration curves were used to calculate the concentrations of the laboratory and field samples. Laboratory recovery and stability was done prior to the field sampling analysis and demonstrate stability of the analyses.



**Figure 1.** Concentration buildup of main VOCs from three different type of stored wood pellets that are commonly used in the Northeastern, US. Pellets were stored for a month in sealed 20 gallon drums containing ~18 kg of pellets.

**Table 1.** Mean, Maximum (plateau) Gas Concentration ( $C_{i,\infty}$ ), Reaction Rate Constant ( $k_i$ ), and Emission Rate (ER) for the Main VOCs Found in Three Different Wood Pellets Stored in Steel Barrels under Room-Temperature (22 °C) Conditions

compound	type of pellets	mean, maximum	$C_{i,\infty}$ (ppb)	$k_i$ (day <sup>-1</sup> )	ER <sub>Total</sub> (mg/kg-day)
methanol	HW	42 ± 20, 126	68 ± 8	0.06 ± 0.02	5.5 × 10 <sup>-5</sup>
	SW	149 ± 70, 262	392 ± 25	0.034 ± 0.003	1 × 10 <sup>-1</sup>
	blended	121 ± 45, 37	175 ± 4	0.107 ± 0.007	1 × 10 <sup>-4</sup>
pentane	HW	2.3 ± 0.3, 3	2.58 ± 0.05	0.26 ± 0.03	2.19 × 10 <sup>-5</sup>
	SW	3 ± 1, 5	5.1 ± 0.2	0.071 ± 0.005	3.7 × 10 <sup>-5</sup>
	blended	3 ± 1, 5	4.25 ± 0.07	0.18 ± 0.01	3.28 × 10 <sup>-5</sup>
pentanal	HW	23 ± 5, 30	25.4 ± 0.3	0.38 ± 0.03	2.12 × 10 <sup>-3</sup>
	SW	11 ± 3, 16	13.7 ± 0.6	0.14 ± 0.02	1.97 × 10 <sup>-2</sup>
	blended	19 ± 3, 24	21.1 ± 0.4	0.30 ± 0.03	2.04 × 10 <sup>-2</sup>
hexanal	HW	3 ± 1, 4	3.60 ± 0.07	0.37 ± 0.05	3.53 × 10 <sup>-5</sup>
	SW	1.4 ± 0.2, 2	1.37 ± 0.06	0.8 ± 0.3	7.12 × 10 <sup>-5</sup>
	blended	2.0 ± 0.3, 3	2.05 ± 0.06	0.9 ± 0.2	3.77 × 10 <sup>-5</sup>

## RESULTS AND DISCUSSION

**VOCs Off-Gassing Kinetics.** Figure S2 shows the mean concentrations of the four major VOCs species, hexanal, pentanal, pentane, and methanol in the drums after their accumulation over 31 days. Mean values were found to be softwood (SW): 412 ± 25; blended: 203 ± 4; hardwood (HW): 99 ± 8, ppb). The pairwise differences among the three pellet types were examined using a 2-sided *t* test. The results showed

that total VOCs (TVOCs) concentrations were different for each pairwise comparison. The most similar pair was softwood (SW) and blended, and these were statistically different ( $p < 0.02$ ).

Figure 1 shows the time-dependent behavior (buildup) of these compounds. The data were well fit by a positive exponential function rising to a maximum. Because there may be multiple mechanisms for the formation/degradation of VOCs, a reasonable approximation for the emission rate is a first order

**Table 2. Maximum (plateau) Gas Concentration, Reaction Rate Constant ( $k$ ), and Emission Rate (ER) for the Four Major VOCs Emitted from Hardwood Pellets Stored in Steel Drums for the Three Different Temperature Conditions<sup>a</sup>**

compounds	temperature (°C)	$C_{i,\infty}$ (ppb)	$k_i$ (day <sup>-1</sup> )	ER <sub>Total</sub>
methanol	6–8	not fitted	$9.60 \times 10^{-5} \pm 1 \times 10^{-2}$	$9.1 \times 10^{-5}$
	22	$20 \pm 2$	$0.21 \pm 0.09$	$4.5 \times 10^{-5}$
	30	$50 \pm 6$	$0.26 \pm 0.09$	$6.5 \times 10^{-5}$
pentane	6–8	$197 \pm 200$	$0.009 \pm 0.009$	$4.1 \times 10^{-4}$
	22	$36 \pm 3$	$0.2 \pm 0.1$	$1.5 \times 10^{-4}$
	30	$105 \pm 11$	$0.20 \pm 0.05$	$2.7 \times 10^{-4}$
pentanal	6–8	ND	ND	ND
	22	$7.1 \pm 0.5$	$0.18 \pm 0.06$	$8.7 \times 10^{-5}$
	30	$12 \pm 2$	$0.3 \pm 0.1$	$9.4 \times 10^{-5}$
hexanal	6–8	$1.8 \pm 0.3$	$0.08 \pm 0.02$	$5.8 \times 10^{-5}$
	22	$26 \pm 2$	$0.12 \pm 0.3$	$1.7 \times 10^{-4}$
	30	$49 \pm 8$	$0.3 \pm 0.1$	$2.1 \times 10^{-4}$

<sup>a</sup>ER-refers to emission rate at mg/kg-day; ND-refers to not detected.

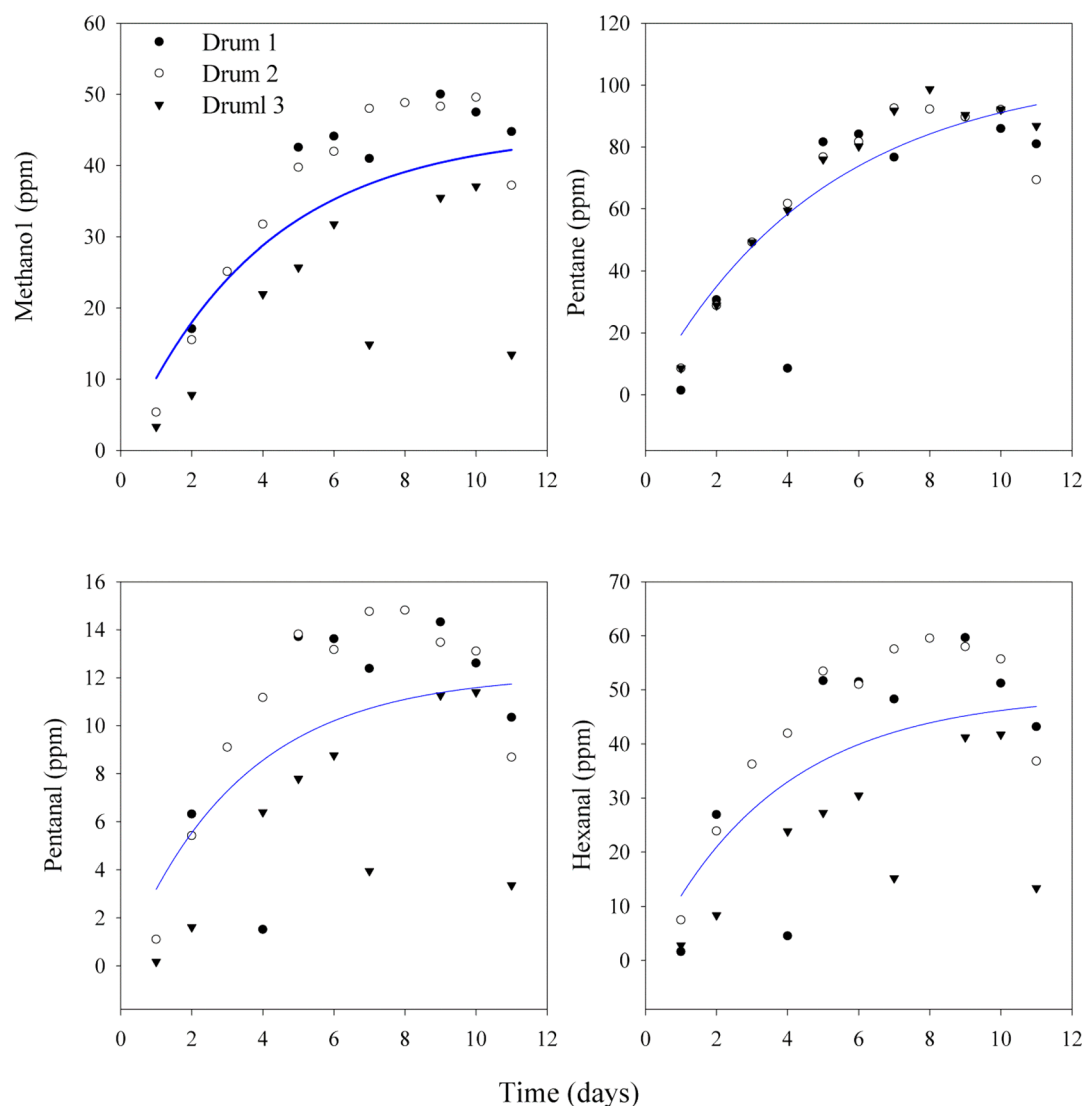
reaction. Based on prior research, this approximation is reasonable because wood decomposes into CO, CO<sub>2</sub>, CH<sub>4</sub>, and VOCs under constant temperature and pressures.<sup>24</sup> The VOC concentrations can be estimated from the following equation:

$$C_i(t) = C_{i,\infty}[1 - \exp(-k_i t)] \quad (1)$$

where  $C_{i,\infty}$  (ppb) represents the maximum constant concentration at the plateau,  $k_i$  the kinetic rate constant (time<sup>-1</sup>) of the first order kinetic equation, and  $t$  is the time of storage (days). An emission factor or rate (ER<sub>i</sub> - in mg of gas per kg materials per day) for each species can be elucidated from the following equation:

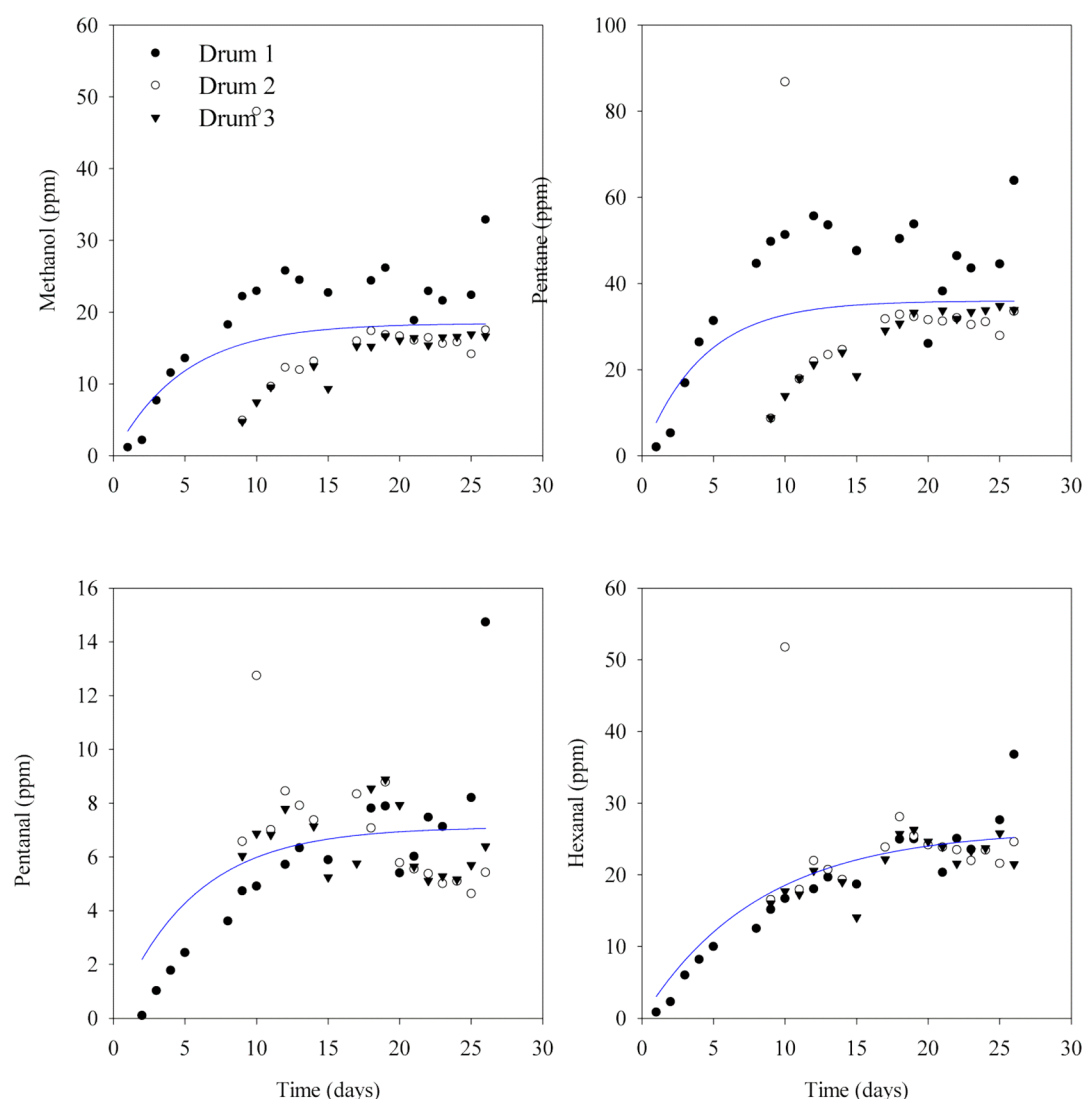
$$ER_i \text{ (mg/kg-day)} = P(C_i V) / (M_{wt} R T M_p) \text{-(day)}$$

where  $R$  is the gas constant,  $M_{wt}$  is the gas molecular weight (gram per mole),  $M_p$  is the total mass of material in the container (kg),  $V$  is the total gas volume in the reactor (cubic meter), and  $P$  is the pressure in the barrel and is approximated as a constant.<sup>24</sup> The volume of gas and pellets was calculated as discussed by Kuang et al.<sup>24</sup> and Fan and Bi.<sup>25</sup>  $C_i$  represents the concentration of each VOC measured every day. The ER



**Figure 2.** Concentration as a function of time for main VOCs found in stored hardwood pellet under heated condition ( $\sim 30$  °C). Drums 1, 2, and 3 represent triplicate experiments for the same conditions.





**Figure 3.** Concentration as a function of time for main VOCs found in stored hardwood pellet under room-temperature condition ( $\sim 22^\circ\text{C}$ ). Drums 1, 2, and 3 represent triplicate experiments for the same conditions.

calculated in this study is expressed as total emission rate ( $ER_{\text{Total}}$ ), and it was calculated by summing the individual ERs per day (Tables 1 and 2).

The VOCs (Figure S1 and Table S1) found emitted by the wood pellets under study were the following:

- SW- acetaldehyde, methanol, acetone, isopropyl alcohol, pentane, pentanal, heptane, hexanal, octane, 2-heptanone,  $\alpha$ -pinene,  $\beta$ -pinene
- HW- methanol, pentane, pentanal, and hexanal.

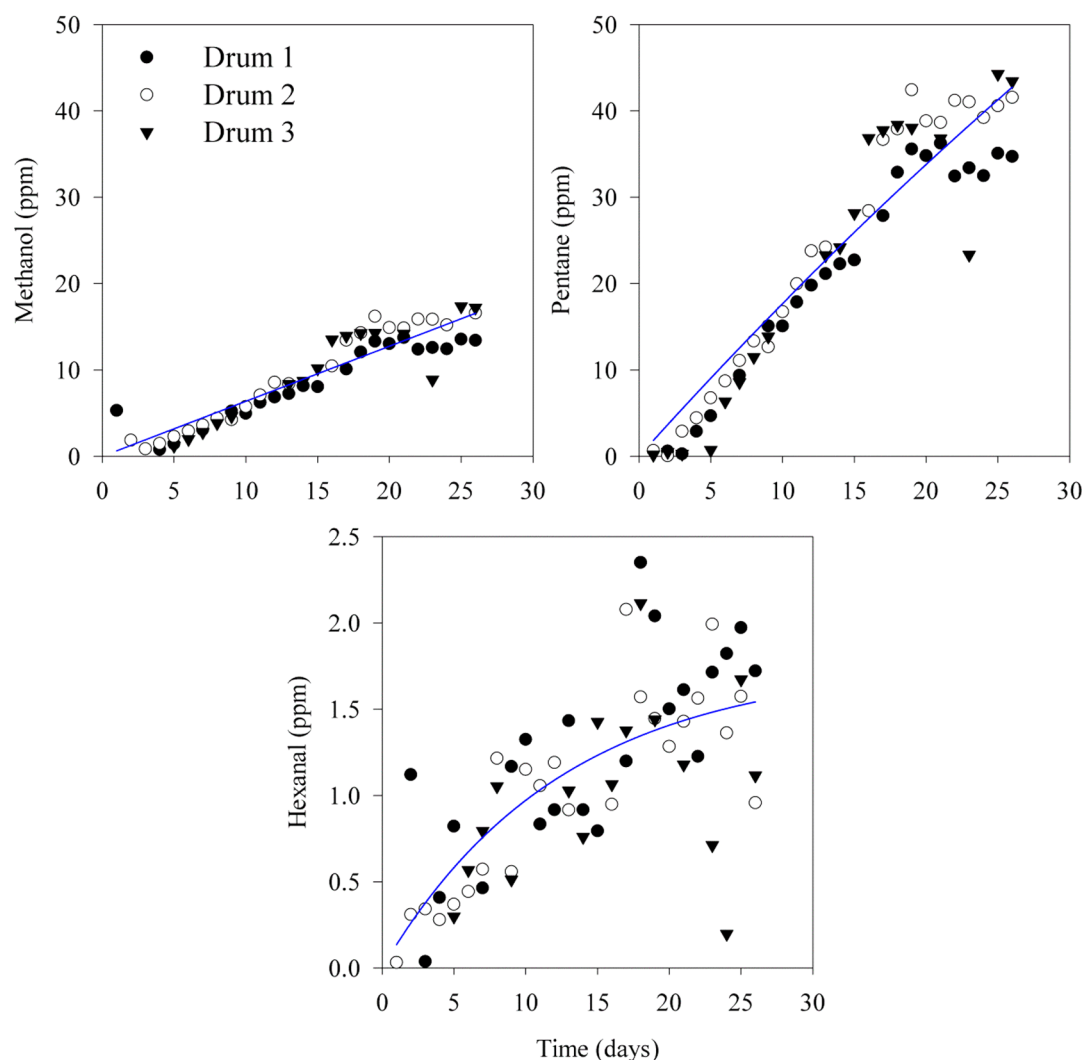
However, the predominant peaks for both types of pellets were hexanal, pentanal, and methanol. Alkanes, alcohols, terpenes, aldehydes, acetone, and benzene were detected and are consistent with previous research of wood pellets VOC emissions.<sup>5,21</sup>

Tables 1 and 2 show the results obtained from above equations. ERs are expressed in mg/kg-day and were found to range from  $10^{-1}$  to  $10^{-5}$ . The reported emission rate for total VOCs (TVOCs) was the sum of the four individual compounds for each type of wood. It was found that the ER of TVOCs from SW ( $6.4 \times 10^{-2}$ ) is higher than blended ( $1.8 \times 10^{-2}$ ) and HW ( $1.6 \times 10^{-2}$ ) mg/kg-day. The more detailed view of the ER as a function of time (Figure S3) shows that methanol has a higher emission in SW. For HW (4 days)

and blended (7 days), methanol reaches a plateau faster than for SW (almost 20 days). Pentanal reached the plateau in the shortest time (5 days) for HW and blended, but it required 7 days for SW. Pentanal has higher emissions in SW, with similar emissions for both HW and blended. Hexanal has a similar pattern as pentanal, but the ERs are approximately 3 orders of magnitude lower.

Pentane in SW increased linearly reaching a plateau in more than 20 days. Thus, its emission may be the result of a different mechanism than the aldehydes. However, in HW and blended pellets, pentane was found to follow an exponential rise and reached a plateau in approximately 10 days. Prior studies have not identified pentane in the VOCs from pellets. The reasons for this difference are unclear.

Methanol had been previously found as natural product of wood<sup>28</sup> as well as being emitted during the manufacture of wood pellets.<sup>5</sup> Figure 1 shows that for methanol, the plateau concentration (a steady maximum concentration) was not fully attained even though the exponential rise function provided a good fit to the data. Thus, methanol formation appears to be slower or its release to the atmosphere is slower than the observed carbonyl compounds. Further studies of the mechanisms that



**Figure 4.** Concentration as a function of time for main VOCs found in stored hardwood pellet under cold condition ( $\sim 6^\circ\text{C}$ ). Drums 1, 2, and 3 represent triplicate experiments for the same conditions.

result in the formation of VOCs will be needed to understand the differing behaviors observed for the various organic compounds.

Emission rates provide insight into mechanisms that produce the VOCs. Aldehydes (pentanal and hexanal) are assumed to be oxidation products of fatty acids in the wood, as previously reported.<sup>5,6,21</sup> Emission occurs faster in HW and blended than SW. According to the manufacturer, softwoods pelletize better thereby producing more compact pellets than HW (Curran Renewable Fuels, Inc., private communication). The more compact surface may reduce the surface area that was previously seen to be important in the rate of CO off-gassing.<sup>23</sup>

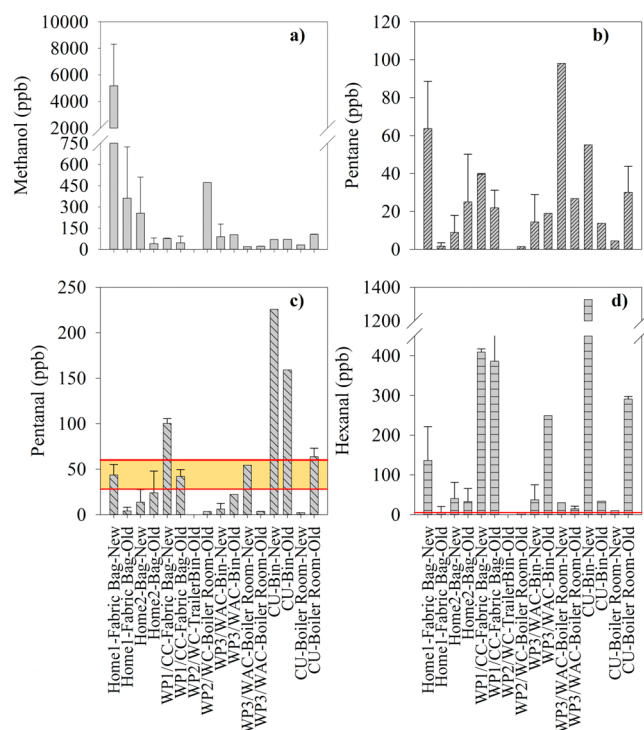
In terms of the TVOCs, SW pellets reach the higher maximum concentration at the plateau (SW:  $412 \pm 25$ ; blended:  $203 \pm 4$ ; HW:  $99 \pm 8$ , ppb). Forest residue storage in lab scale vessels produced 85 ppm of TVOCs.<sup>29</sup> Our results show much lower concentrations, 2 to 3 orders of magnitude, possibly because of variations in storage vessel volume, temperature, and moisture content between the two studies and possibly an influence by the manufacturing process of the pellets. However, as of now, we do not have any direct evidence of VOC reduction by pellet manufacturing processes. Also, these results show that pentanal (15–50% of TVOCs) is more abundant than

hexanal (2–10%), probably due to the wood mix used for pellets in this area. Previous study showed hexanal (70–80% w/w) as the dominant species.<sup>5</sup>

Emissions under different temperature conditions are presented in Figures 2–4. ERs are of the order of  $10^{-4}$  to  $10^{-5}$ . It is observable that at higher temperatures, the concentrations reached a higher plateau value faster than at lower temperatures. The pellets exposed to colder temperatures attained lower concentrations and showed much slower rises in concentrations. Emitted CO and CO<sub>2</sub> followed a similar pattern.<sup>16,23</sup> The difference in ERs between the HW pellets from Tables 1 (older) and 2 (2–10 days old) are due to the aging of the pellet surfaces in storage leading to lower emission rates.

## ■ VOCS FROM STORED WOOD PELLETS IN HOMES AND WORKPLACES

VOCs were measured in homes and workplaces (WP) that used wood pellets for heating during the winter season of 2014–15 (Figure 5; Table S2). In general, the concentrations for all of the VOCs never exceeded the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV)<sup>30</sup> (Table S3) and were more than 3 orders of magnitude lower than laboratory and field values. Field samples



**Figure 5.** TVOCs concentration from stored wood pellets at homes and work places (WP) collected during the heating season (2014–2015). WP refers to work place; CC - Chamber of Commerce; WC - Wild Center; WAC - Walker Center; CU - Clarkson University; EC - Energy Cabin. The horizontal lines represent odor threshold values. Note: Odor thresholds can be an important indicator of occupant impact for pentanal ranges from 28 to 60 ppb and hexanal is 4.5 to 5 ppb.

ranged from  $67 \pm 8$  to  $5000 \pm 3000$  ppb of TVOCs and from  $\sim 12$  to 1500 ppb of aldehydes. Figure 5 shows that the highest concentrations were found for methanol at home 1. Typically, the concentrations of the VOCs decreased after 2–5 weeks (old) of pellet aging consistent with Arshadi et al.<sup>6</sup> Although the mechanism for the emission of carbon monoxide and VOC (intermediate to the CO emission) is not fully understood at this time, we and other researchers have demonstrated that ER of VOCs and CO decrease over time. The likely emission rate reduction is correlated with the availability of materials, such as hemicellulose and fatty acids, to oxidize. The surface area of the pellets and the ability of oxygen to permeate the mass of pellets likely play a role in the emission rates as well.<sup>6,23</sup>

However, elevated levels of VOCs were observed in the homes and were likely from other sources in the buildings such as cooking, air fresheners, garages,<sup>8</sup> cleansers, disinfectants, paints and coatings, wallpaper, laminate floorings, among others.<sup>10,31,32</sup> In the boiler room for one sample, there are high concentrations of pentane, pentanal, and hexanal. These species could be due to infiltrations from a storage bin. Odor thresholds can be important indicators of occupant discomfort and irritation. Methanol and pentane have odor thresholds in the ppm range and thus are not a factor in this study. The odor thresholds for pentanal (28 to 60 ppb) and hexanal (4.5 to 5 ppb) were exceeded in a number of the samples. Pentanal concentrations were measured in the 280 to 600 ppb range. The hexanal concentration can be of concern because previous research shows that the odor threshold is 25 ppb, and sensory irritation was reported at 281 ppb.<sup>33</sup> The hexanal odor threshold was exceeded in one home and in the WP/CC site. The hexanal

concentration reached  $\sim 400$  ppb for fresh and old pellets. The highest concentrations were observed coming from the fabric bags (Figure 4). Home 1 reported that ventilation was applied at their site due to odors and discomfort (allergic reactions). This response is likely to be due to the aldehydes.

A prior field study measured aldehydes from wood pellets in a domestic storage room and found a mean concentration of  $\sim 20$  mg/m<sup>3</sup>, with the highest peak at 98 mg/m<sup>3</sup> after 18 h of fresh delivery.<sup>5</sup> Our results show much lower concentrations ( $\sim 3$  orders of magnitude). The difference between concentrations observed in this study and earlier results could be due to different types of wood in the pellets. The emissions of aldehydes and ketones are significantly lower when pellets are made from spruce than pine due to the lower amount of fatty acids in spruce.<sup>5</sup>

The emission of VOCs occurs in parallel with carbon monoxide and has been demonstrated in a number of previous studies in the literature.<sup>3,16–19,21,23</sup> In the work presented here, the concentration of CO and VOCs rise to a plateau in the laboratory experiments at similar times, usually within a few days of each other. The emission of VOCs occurs in parallel with carbon monoxide and has been demonstrated in a number of previous studies in the literature.<sup>2,12–15,23</sup> In the work presented here, the concentration of CO and VOCs plateau in the laboratory experiments at similar times, usually within a few days of each other. However, temperature and moisture content can change the emission rates of both the VOCs and CO, yet not in linear relationship for all species of VOCs. As the mechanism(s) of emission of VOCs and CO from wood pellets are further explored, the timing of peak emission rates and factors that influence evolution of the compounds from the pellets may become more evident. However, temperature and moisture content can change the emission rates of both the VOCs and CO, but not resulting in linear relationships for all of the VOC species. The mechanism(s) of VOCs and CO emissions from wood pellets require further exploration that may identify the factors that govern the nature and rate of evolution of compounds from the pellets.

## CONCLUSIONS

The results of this study demonstrate that VOCs are off-gassed from stored wood pellets. Laboratory study show the main VOCs produced due to the oxidation of store wood pellets are methanol, pentane, pentanal, and hexanal. Higher concentrations but lower emission rates were found from softwood followed by blended and hardwood pellets, respectively. Lower temperatures reduced the emission rates and the maximum concentrations of these gases. Also, aging of the pellets reduced the VOCs concentrations. Storage of pellets considering these factors (aged and temperature) can be considered to reduce the emission of VOCs when the pellets are distributed to the end-users.

VOC concentrations in occupational settings from our field work never exceeded appropriate Threshold Limit Value (TLV) guidelines, but the odor thresholds for pentanal were exceeded after the fresh pellet delivery. Hexanal odor and sensory irritation levels were exceeded, suggesting the need of improving ventilation in store rooms to mitigate short-term impacts of aldehydes coming from stored wood pellets. As recommended by earlier studies, the use of natural ventilation, such as windows, fans, tubes that connect the store room with the outside air<sup>34</sup> can reduce the concentration of these VOCs. Extensive further study is needed of the effects of temperature, cross-ventilation, type of storage, room volume, and pellet age

so that they can be taken into account in developing recommendations of a storage room design and proper ventilation in domestic and commercial buildings using pellet boilers.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b01398.

Chromatograms for typical softwood and hardwood samples; average VOC concentrations; concentration as a function of time plots for the four major VOC species; lists of VOCs and their concentrations; occupational exposure limits and health effect of major VOCs off-gassed from wood pellets (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [hopkepk@clarkson.edu](mailto:hopkepk@clarkson.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by New York State Energy Research and Development (NYSERDA) under Contract 32973. The authors thank Curran Renewable Energy LLC for the donation of the wood pellets used in this study. Also, we want to acknowledge the Wild Center Museum, the Massena Chamber of Commerce, and all of the people who allowed us to enter into their homes and collect samples.

## ■ REFERENCES

- (1) U.S. Census Bureau. HOUSE HEATING FUEL. Universe: Occupied housing units, 2012 American Community Survey 1-Year Estimates. Available at [http://factfinder.census.gov/faces/tableservices/jsf/pages/productview.xhtml?pid=ACS\\_12\\_1YR\\_B25040&prodType=tabl](http://factfinder.census.gov/faces/tableservices/jsf/pages/productview.xhtml?pid=ACS_12_1YR_B25040&prodType=tabl).
- (2) U.S. Energy Information Administration (EIA). Details of the winter outlook for individual fuels: Wood. Available at: [http://www.eia.gov/todayinenergy/detail.cfm?id=13311#tabs\\_SpotPriceSlider-5](http://www.eia.gov/todayinenergy/detail.cfm?id=13311#tabs_SpotPriceSlider-5) (assessed on 08/28/2015).
- (3) Soto-García, L.; Huang, X.; Thimmaiah, D.; Rossner, A.; Hopke, P. Exposures to Carbon Monoxide from Off-Gassing of Bulk Stored Wood Pellets. *Energy Fuels* **2015**, *29*, 218–226.
- (4) Svedberg, U.; Galle, B. Assessment of terpene levels and workers' exposure in saw mills with long path FTIR. *Appl. Occup. Environ. Hyg.* **2000**, *15*, 686–694.
- (5) Svedberg, U.; Höglberg, H.; Höglberg, J.; Galle, B. Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic hazard. *Ann. Occup. Hyg.* **2004**, *48*, 339–349.
- (6) Arshadi, M.; Geladi, P.; Gref, R.; Fjällström, P. Emission of Volatile Aldehydes and Ketones from Wood Pellets under Controlled Conditions. *Ann. Occup. Hyg.* **2009**, *53*, 797–805.
- (7) Loftness, V.; Hakkinen, B.; Adan, O.; Nevalainen, A. Elements That Contribute to Healthy Building Design. *Environ. Health Perspect.* **2007**, *115*, 965–970.
- (8) Batterman, S.; Jia, C.; Hatzivasilis, G. Migration of volatile organic compounds from attached garages to residences: A major exposure source. *Environ. Res.* **2007**, *104*, 224–240.
- (9) Haghighat, F.; De Bellis, L. Material Emission Rates: Literature Review, and the Impact of Indoor Air Temperature and Relative Humidity. *Building and Env.* **1998**, *33*, 261–277.
- (10) Wolkoff, P. How to measure and evaluate volatile organic compound emissions from building products. *Sci. Total Environ.* **1999**, *227*, 197–213.
- (11) U.S. EPA. *Exposure Factors Handbook (1997 Final Report)*; U.S. Environmental Protection Agency: Washington, DC; Report No. EPA/600/P-95/002F a-c, 1997.
- (12) WHO (World Health Organization), Regional Office for Europe.. *Indoor air quality: organic pollutants. Euro Reports and Studies, No. III*; World Health Organization: Copenhagen, 1989.
- (13) Wolkoff, P.; Clausen, P. A.; Jensen, B.; Nielsen, G. D.; Wilkins, C. K. Are we measuring the relevant indoor pollutants? *Indoor Air* **1997**, *7*, 92–106.
- (14) Wolkoff, P.; Clausen, P.; Wilkins, C.; Hougaard, K.; Nielsen, G. Formation of strong airway irritants in a model mixture of alpha-pinene/ozone. *Atmos. Environ.* **1999**, *33*, 693–698.
- (15) Wolkoff, P.; Nielsen, G. Organic compounds in indoor air - their relevance for perceived indoor air quality? *Atmos. Atmos. Environ.* **2001**, *35*, 4407–4417.
- (16) Kuang, X.; Shankar, T. J.; Bi, X. T.; Lim, C. J.; Sokhansanj, S.; Melin, S. Rate and peak concentrations of off-gas emissions in stored wood pellets—sensitivities to temperature, relative humidity, and headspace volume. *Ann. Occup. Hyg.* **2009**, *53*, 789–796.
- (17) Kuang, X.; Shankar, T. J.; Sokhansanj, S.; Lim, C. J.; Bi, X. T.; Melin, S. Effects of headspace and oxygen level on off-gas emissions from wood pellets in storage. *Ann. Occup. Hyg.* **2009**, *53*, 807–813.
- (18) Svedberg, U.; Samuelsson, J.; Melin, S. Hazardous off-gassing of carbon monoxide and oxygen depletion during ocean transportation of wood pellets. *Ann. Occup. Hyg.* **2008**, *52*, 259–266.
- (19) Svedberg, U.; Petrini, C.; Johanson, G. Oxygen depletion and formation of toxic gases following sea transportation of logs and wood chips. *Ann. Occup. Hyg.* **2009**, *53*, 779–787.
- (20) Granström, K. M. Sawdust age affect aldehyde emissions in wood pellets. *Fuel* **2014**, *126*, 219–223.
- (21) Arshadi, M.; Gref, R. Emission of volatile organic compounds from softwood pellets during storage. *Ann. Occup. Hyg.* **2005**, *55*, 132–135.
- (22) NIOSH Pocket Guide to Chemical Hazards, Appendix: Aldehydes and NIOSH 2018: Aliphatic Aldehydes. Available at <http://www.cdc.gov/niosh/npg/npgd0652.html> (updated: February 13, 2015).
- (23) Soto-Garcia, L.; Huang, X.; Thimmaiah, D.; Denton, Z.; Rossner, A.; Hopke, P. K. An Assessment of Carbon Monoxide Emission Rates from Laboratory Experiments of Wood Pellets from the Northeastern US. *Energy Fuels* **2015**, *29*, 3715–3724.
- (24) Kuang, X.; Shankar, T. J.; Bi, X. T.; Sokhansanj, S.; Jim Lim, C.; Melin, S. Characterization and Kinetics Study of Off-Gas Emissions from Stored Wood Pellets. *Ann. Occup. Hyg.* **2008**, *52*, 675–683.
- (25) Fan, C.; Bi, X. T. Development of Off-Gas Emission Kinetics for Stored Wood Pellets. *Ann. Occup. Hyg.* **2013**, *57*, 115–124.
- (26) Rossner, A.; Farant, J. P.; Simon, P.; Wick, D. P. Development of a Flow Controller for Long-Term Sampling of Gases and Vapors Using Evacuated Canisters. *Environ. Sci. Technol.* **2002**, *36*, 4912–4920.
- (27) U.S. Environmental Protection Agency (USEPA). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed.. Compendium Method TO-15, Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Report No. EPA/625/R-96/010b; Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency: Cincinnati, OH, 1999.
- (28) Guenther, A.; Zimmerman, P.; Wildermuth, M. Natural volatile organic compound emission rates estimates for US woodland landscape. *Atmos. Environ.* **1994**, *28*, 1197–1210.
- (29) He, X.; Lau, A.; Sokhansanj, S.; Lim, C. J.; Bi, X.; Melin, S. Dry matter losses in combination with gaseous emissions during the storage of forest residues. *Fuel* **2012**, *95*, 662–664.



(30) Threshold limit values (TLVs) and biological exposure indices (BEIs). Available at: <http://www.acgih.org/tlv-bei-guidelines/policies-procedures-presentations/overview>.

(31) Jones, A. P. Indoor air quality and health. *Atmos. Environ.* **1999**, *33*, 4535–4564.

(32) Marchand, C.; Le Calvé, S.; Mirabel, P.; Glasser, N.; Casset, A.; Schneider, N.; De Blay, F. Concentrations and determinants of gaseous aldehydes in 162 homes in Strasbourg (France). *Atmos. Environ.* **2008**, *42*, 505–516.

(33) Zheng, L. intensity of odor and sensory irritation as a function of hexanal concentration and interpresentation intervals: an exploratory study. *Perceptual and Motor Skills* **2010**, *111*, 210–228.

(34) Emhofer, W.; Lichtenegger, K.; Haslinger, W.; Hofbauer, H.; Schmutzer-Roseneder, I.; Aigenbauer, S.; Lienhard, M. Ventilation of Carbon Monoxide from the Biomass Pellet Storage Tank-A Study of the Effects of Variation of Temperature and Cross-ventilation on the Efficiency of Natural Ventilation. *Ann. Occup. Hyg.* **2015**, *59*, 79–90.