Emissions of Hexanal and Terpenes during Storage of Solid Wood Fuels

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Abstract

The purpose of this study was to investigate emissions during storage of solid wood fuels by measuring both the emission of monoterpenes and the formation of aldehydes during storage of undried sawdust, dried sawdust, and pellets. Sawdust is commonly stored up to several months at pellet plants. Pellets are stored due to seasonal demand variation and wood fuel trade. Freshly sawn sawdust from Scots pine (*Pinus sylvestris*) was dried and pelleted. The fuel was stored in a controlled laboratory setting to avoid undue influence of temperature and humidity fluctuations. The emission of volatiles was analyzed with static headspace and gas chromatography–mass spectroscopy. The content of terpenes in undried sawdust decreased dramatically in the first days of storage, with 10 percent of the original amount left after 10 days. In dried sawdust, about two-thirds of the terpenes that remained after drying were released in the first 10 days. In sawdust, the hexanal concentration was negligible at first, became equal to the terpene concentration after 15 days, and reached a maximum after 40 to 50 days. Hexanal was then found in an equal amount to the remaining terpene content in undried sawdust; in dried sawdust, it was found in a much higher amount than the remaining terpene content. In pellets, hexanal content was consistently higher than the terpene content. The wood fuels were low-emitting for both terpenes and hexanal after 2 to 3 months. In conclusion, although terpenes have been assumed to be the predominant volatiles emitted during storage of solid wood fuels, hexanal from fatty acid oxidation is also of importance.

The environmental and energy policies in most industrialized nations worldwide aim to replace fossil fuels with renewable sources of energy. Solid biofuels such as wood fuels are an especially promising option since solid biofuels can be used by applying existing technology, can be easily converted into useful energy when needed, and have relatively low costs compared to other renewable energy sources (Kaltschmitt and Weber 2006). In most cases, however, wood-based biofuels must be refined before they can replace fossil fuels. Compared with unrefined wood, wood shavings and sawdust, dried and compressed into pellets or briquettes, have a higher energy density, are easier to transport, have lower emissions of hydrocarbons and particles during combustion (Jonsson and Hillring 2006), take up less room during storage, and are less susceptible to mold and insect attacks, which cause temperature increases in piles (Lehtikangas 2000).

As sawdust supply fluctuates according to sawmill activity, it is a common practice to store sawdust for up to several months at pellet plants. Once produced, pellets may be stored due to seasonal demand variation, and their use can also be delayed due to the wood fuel trade. The dominating compounds released from wood during storage are terpenes and aldehydes. Terpenes are a component of the resin produced by conifers and are released both from conifer trees and from conifer wood (i.e., softwood). Aldehydes, mostly hexanal, are the most significant class of odorous compounds formed due to the auto-oxidation and photo-oxidation of unsaturated lipid compounds (Fig. 1).

In softwoods, many different fatty and resin acids have been identified. The predominant unsaturated fatty acid in Scots pine (*Pinus sylvestris*) and in Norway spruce (*Picea abies*) is oleic acid (18:0, *n*-9), and the next most dominant fatty acids are linoleic acid (18:2, *n*-6) and α-linolenic acid (18:3, *n*-3) (Arshadi and Gref 2005). Auto-oxidation of unsaturated fatty acids is a complex self-catalyzing free radical chain reaction (Porter et al. 1995), a process commonly referred to as the fats going rancid. It is likely that the lipid oxidation starts after sawing, as damage to cells causes lipids to hydrolyze to free lipid acids, which are more easily oxidized. Free radicals can be produced by light photons or by metal ions or by the spontaneous reaction of oxygen that has material with a readily abstractable hydrogen. When the oxidation has started, it self-catalyzes and continues until all the radicals have been neutralized.

Knowledge of emissions from sawdust and pellets is needed to estimate worker exposure, exposure from indoor pellets storage, contribution to ground-level ozone forma-
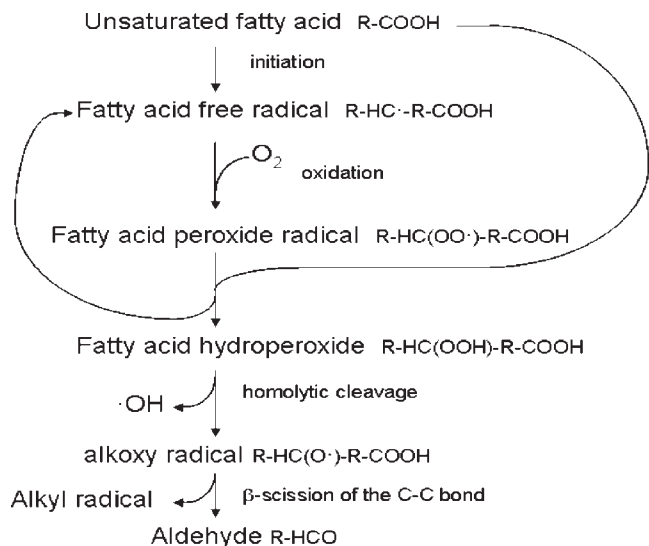
Figure 1.—Principle path of fatty acids auto-oxidation.

tion, risk of unpleasant and noxious odors from wood pellets, and risk of pellet self-ignition.

Terpenes and hexanal have adverse health effects. Monoterpenes irritate mucous membranes, affecting the eyes and the respiratory system (Hedenstierna et al. 1983). A hexanal exposure of 10 ppm causes ocular and nasal discomfort and results in headaches (Ernstgard et al. 2006). The occupational exposure limit for terpenes is 25 ppm in Sweden, Norway, Denmark, and Finland, and 100 ppm in the United States (set by the Occupational Safety and Health Administration). Hexanal has been detected in domestic pellet storage rooms—the emissions varied with ambient temperature and peaked after 2 months of storage during warm weather (Svedberg et al. 2004). The released compounds also have an environmental impact—in the presence of nitrogen oxides both terpenes and aldehydes contribute to the formation of ground-level ozone and other photochemical oxidants, which disturb plant photosynthesis, thereby causing forest and crop damage (Reich and Amundson 1985). High levels of volatile aldehydes emitted from pellets are responsible for a pungent smell (Arshadi and Gref 2005), which can cause consumer dissatisfaction. Fatty acid oxidation has also been identified as a cause of spontaneous self-ignition of pellets, which have caused fires in silos (Persson and Blomqvist 2009).

Previous research on the storage of solid biofuels from conifer wood has mostly focused on substance loss or on moisture and temperature profiles within piles of logging residues (Thörnqvist 1985, Jirjis and Theander 1990, Nurmi 1999) or pellets (Lehtikangas 2000). In addition, the aldehydes emitted from wood pellets have been analyzed (Arshadi and Gref 2005), and the emissions of terpenes and polyaromatic hydrocarbons from piles of wood chips exposed to temperature and humidity variations have been measured (Rupar and Sanati 2005).

The emissions from wood during storage are affected by previous processing. The terpenes are emitted from fresh sawdust, during drying, from dry sawdust, during pelleting, and from pellets. Earlier research on lipid oxidation during pelleting has concluded that it is imperative to ascertain when the oxidation process starts (Arshadi and Gref 2005). Therefore information on emissions from the same batch of sawdust during the entire pellet production process would be particularly valuable.

The objective of this study was to take a comprehensive approach to the emissions of volatile compounds during storage of wood fuel and wood fuel raw materials, by measuring both the emission of monoterpenes and the formation of hexanal during storage of undried sawdust, dried sawdust, and wood pellets. This was done in a controlled laboratory setting to avoid undue influence of temperature and humidity fluctuations.

Materials and Methods

Materials

Fresh sawdust from Scots pine was collected from a nearby sawmill that uses frame saws. Most wood fuel pellets are made from Scots pine or Norway spruce. Scots pine was chosen since pine sawdust contains considerably more fatty acids than spruce does, making problems with fatty acid oxidation more prevalent with pine pellets.

The raw material used for the production of pellets was sawn and collected on November 30, 2007, from a nearby sawmill and strained to remove large chunks of bark and wood. Undried sawdust had a moisture content of 60 percent. It was dried in a continuous spouted bed dryer with recirculating drying medium to a moisture content of 14.3 percent. The inlet temperature was 200°C to 240°C and the outlet temperature was 115°C to 135°C. Pellets were made 5 days after drying in an Amandus Kahl C33-390 with a die for 8-mm pellets. The die pressure was set at 85 bar and the die temperature was kept at 90°C to 115°C. The moisture content of the pellets was 8.1 percent.

In addition, analyses of the emissions during storage of fresh sawdust were made on sawdust produced and collected February 22, 2008. The undried sawdust had a moisture content of 61 percent.

Methods

The undried sawdust, dried sawdust, and pellets were stored indoors at 18°C in cardboard cylinders with a diameter of 10 cm and a height of 1 m. Samples were removed for testing through an outlet placed halfway between the top and bottom of the cylinder.

Samples were analyzed by static headspace gas chromatography (SHS-GC), a technique that is often used to determine aldehydes formed during lipid oxidation (Frankel et al. 1989, Löliger 1990). In static headspace, the sample undergoing investigation is sealed in a vial in which equilibrium is reached between volatiles in the sample and in the headspace air of the vial. The sample is heated to enrich the headspace with volatiles. A portion of the headspace air is then injected into a gas chromatograph.

The samples, about 1 g of sawdust or pellets, weighed with 0.00005 g exactness, were put into 20-ml headspace vials and covered with 5 ml of water. The vials were closed with heat-resistant PTFE-coated silicone rubber septa and crimp caps and heated for 30 min at 80°C in a heat block. Thereafter, 1 ml of the gas in the vial (the headspace gas) was injected into a gas chromatograph. Three vials were analyzed for each sample time and material.

The gas chromatograph was a Perkin Elmer AutoSystem fitted with an unpolar capillary column (J&W Scientific, DB5-MS, 30 m by 0.25 mm). The column was temperature programmed as follows: held at 40°C for 2 min, increased
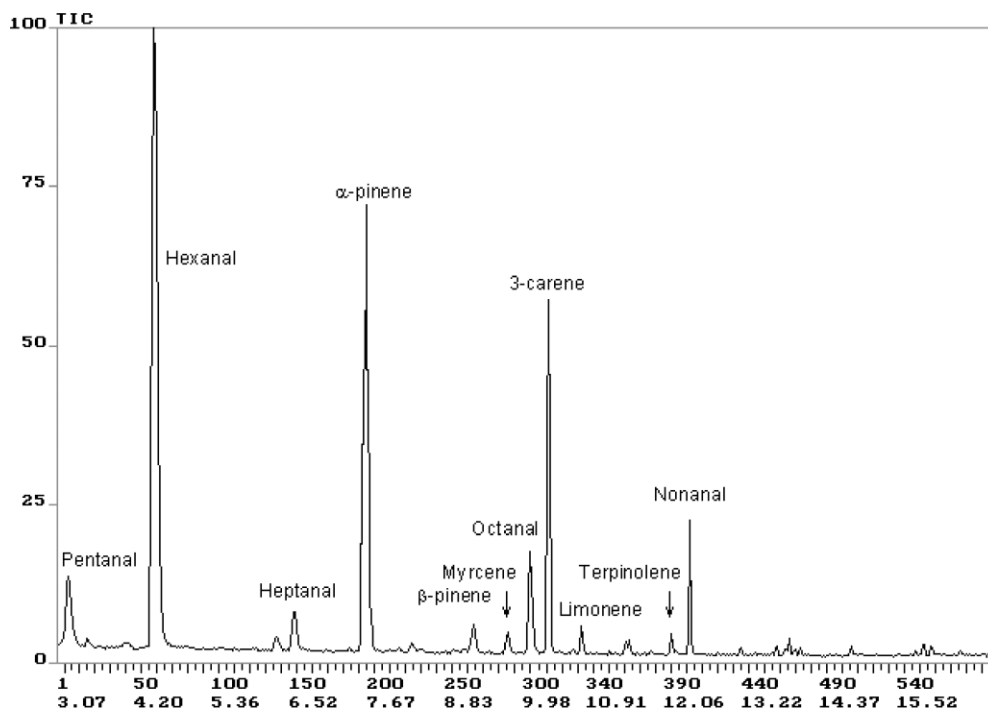
Figure 2.—Gas chromatogram acquired via static headspace vapor sampling from undried sawdust stored for 39 days. The x axis shows the retention time in minutes and the mass spectrometer scan number. The y axis shows the total ion count (TIC) as measured by the mass spectrometer.

by 15°C/min to 70°C, held at 70°C for 5 min, increased by 15°C/min to 200°C, and held at 200°C for 7 to 25 min. The injector temperature was 200°C. The carrier gas was helium. The detector was a mass spectrometer, a Perkin-Elmer Qmass 910 that uses electron ionization. It was in total ion chromatogram mode and set to scan from 45 to 300 m/e, an interval that included all ion fragment peaks of interest. The gas chromatography–mass spectroscopy (GC-MS) detection limit was 0.2 mg/m^3.

The detected substances and their separation can be seen in Figure 2, which shows the gas chromatogram acquired via static headspace vapor sampling from undried sawdust stored for 39 days. The substances of interest were identified by comparing retention times with those of authentic reference compounds and from their mass spectra. The compounds were quantified using calibration curves. Individual authentic response factors were used for all monoterpenes and for hexanal. The calibration curves had an R^2 of 0.85 to 0.94. Reference compounds were obtained from Sigma-Aldrich. All chemicals used were analytical grade.

The SHS-GC-MS procedure was validated by analyzing five vials of pellets stored for 20 days, and reasonably good precision was achieved (Table 1).

The ovendry weight (ODW) of the wood was determined as the weight after drying at 103 ± 2°C until constant weight was reached. The wood moisture content is expressed as wet basis.

Results and Discussion

Fresh sawdust

Freshly sawn sawdust contained about 1 g of terpenes per kilogram of ODW. The terpenes found were α-pinene, β-pinene, myrcene, 3-carene, limonene, and terpinolene. The monoterpenes had a composition typical of Scots pine, as can be exemplified with the fresh sawdust from day 0: of the monoterpenes, 72 percent were α-pinene; 3 percent, β-pinene; 0.9 percent, myrcene; 23 percent, 3-carene; 0.8 percent, limonene; and 1.1 percent, terpinolene.

The content of terpenes in the fresh undried sawdust decreased dramatically in the first days of storage, with roughly 10 percent of the original amount left after 10 days (Fig. 3). The speed of the process is likely due to the small volume and large area of sawdust particles. Regarding the time it took for the terpene content to reach very low levels, there was a difference between the November and February sawdust, with February having very low amounts left after 20 days and November reaching this point after 60 days. The lowest terpene level measured was 25 mg/kg ODW.

At first there was no hexanal in the sawdust, which is to be expected since it would take some time for the oxidation process to begin. The lack of hexanal at 0 days of storage shows that initiation and thermal decomposition of hydroperoxides did not take place during the headspace equilibration period. Hexanal was measurable after 10 days

Table 1.—Analysis of volatiles from pellets stored at 18°C for 20 days.[a]

Volatiles	n	Average	Variance	SD	CV (%)
Hexanal	5	26	8.3	2.9	11
Heptanal	5	1.9	0.045	0.21	11
α-Pinene	5	2.1	0.13	0.37	17
3-Carene	5	0.76	0.021	0.15	19
Terpene sum	5	2.9	0.26	0.51	17

[a] Results are expressed as mg/kg ODW. n = number of samples. Precision is shown by the variance, standard deviation (SD), and the coefficient of variation (CV).
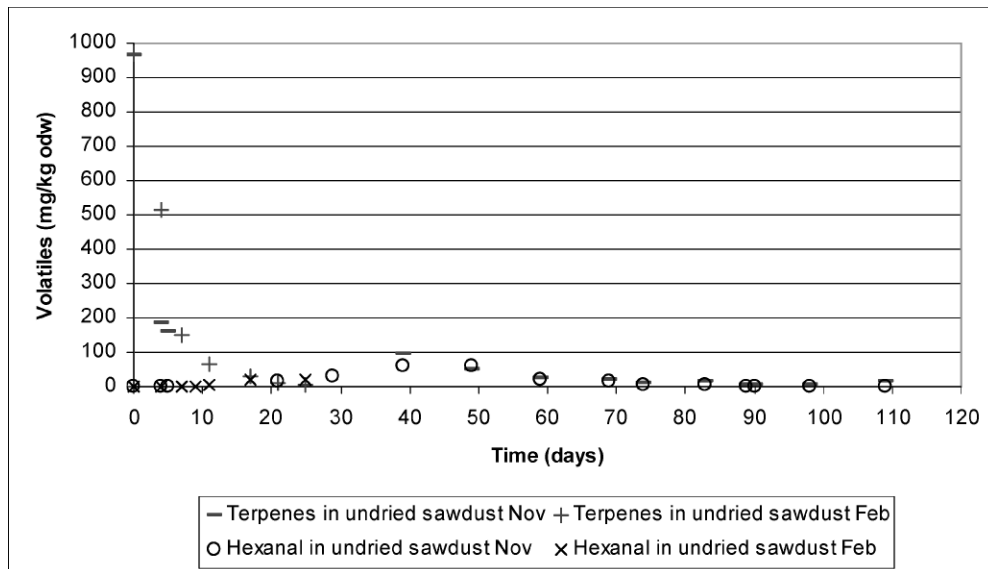
Figure 3.—Monoterpenes and hexanal in undried sawdust during storage.

and the fatty acid oxidation reached a maximum after 40 to 50 days (at 60 mg/kg), at which time the amount of hexanal in the sawdust was about equal to the remaining terpene content in the November sawdust (Fig. 3). As the radical concentration increases, the number of termination reactions increases, unless mobility of free radicals is impeded. As a result, hexanal formation decreases after a time. After 2 months, the hexanal content in the wood stabilized at about 20 mg/kg ODW.

Dried sawdust

Most of the terpenes in the sawdust were released during drying. After the sawdust had been dried, 50 mg/kg ODW were left in the sawdust. The composition of monoterpenes was unaffected. About two-thirds of the remaining terpenes were released in the first 10 days of storage, and the terpene content then remained constant during the next 50 days (Fig. 4).

Hexanal was formed after about 15 days and was at a maximum after 40 to 50 days of storage, at 144 mg/kg ODW (Fig. 4). During the time when fatty acid oxidation (hexanal production) peaked, the amount of hexanal in the sawdust was much higher than the amount of terpenes. Both terpenes and hexanal were mostly emitted after slightly fewer than 3 months of storage. At that time, the content of hexanal was 3 mg/kg ODW and that of terpenes was 1 mg/kg ODW.

The formation of hexanal was similar in time frame but higher in amount in the dried sawdust compared with the undried sawdust. The higher amount of hexanal indicates a higher concentration of free radicals in the system, considering the free-radical nature of the oxidative reactions. The larger hexanal content could also be due to a
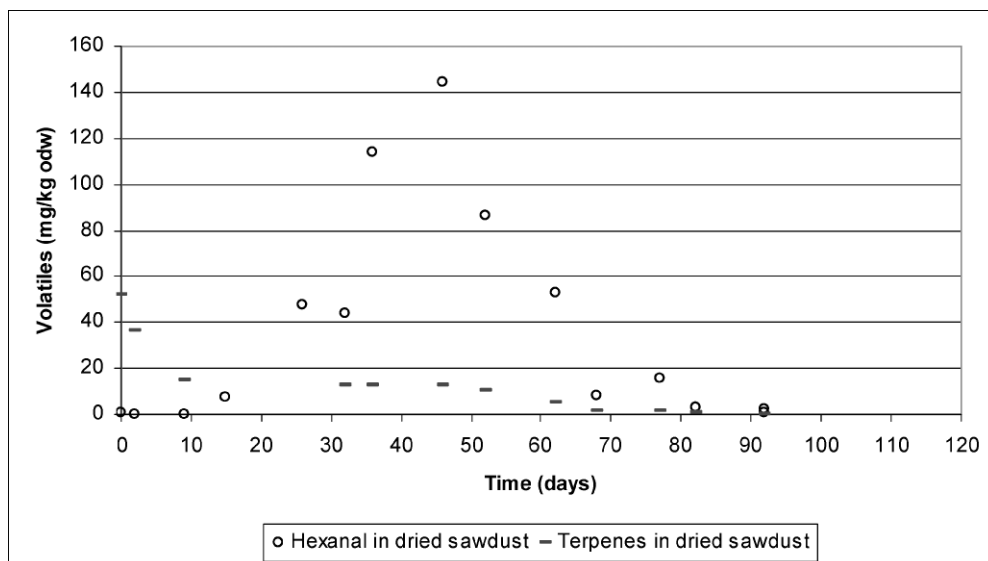

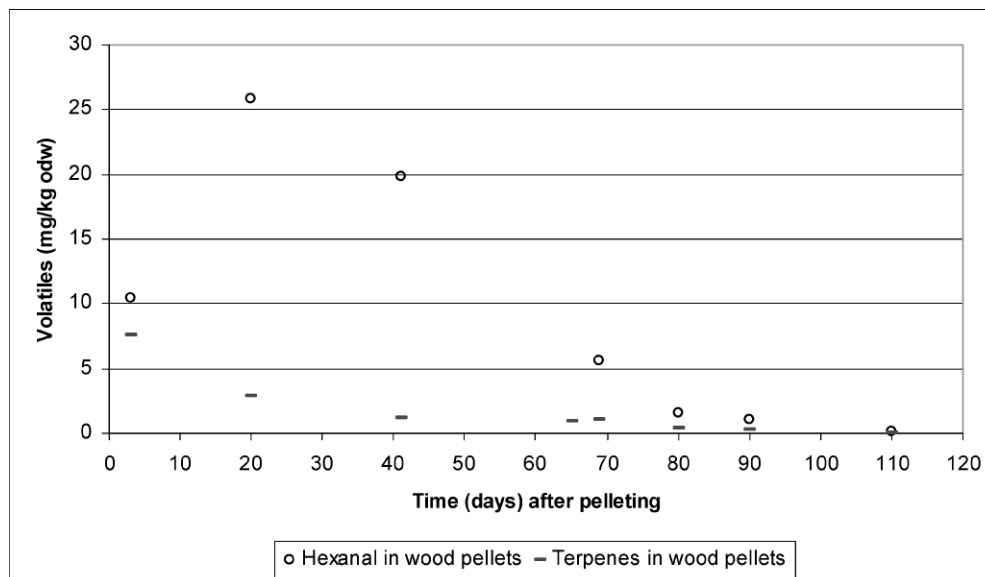*Figure 4.—Monoterpenes and hexanal in dried sawdust during storage.*

Figure 5.—Monoterpenes and hexanal in pellets during storage.

higher amount of free fatty acids, possibly due to damage to wood cells during drying.

Pellets

The terpene levels in the pellets were very low because terpenes had been emitted both in the drying and in the pelleting processes. The only terpenes present in measurable amounts were α-pinene and 3-carene. Terpenes were still being emitted, however, as the amount of terpenes decreased even more during storage (Fig. 5). The amount of terpenes in this batch of pellets was unusually low, as a more common amount of terpenes in pellets is about 100 mg/kg ODW (Ståhl et al. 2004).

Hexanal was found after only a few days of storage, which is a more rapid progression than in sawdust. This shows that the process of drying and pelleting hastens hexanal formation. The faster formation of hexanal in pellets may be due to an accumulation of semistable fatty acid hydroperoxides during the propagation stage of auto-oxidation, as seen in model studies (Chan 1987). When sawdust has been dried and pelleted, the extractives have been exposed to both oxygen and high temperatures and are likely to contain fatty acid hydroperoxides as well as unsaturated fatty acids.

The hexanal content in the pellets increased quickly to reach a maximum 25 days after drying (20 days after pelleting), at 26 mg/kg (Fig. 5). The hexanal then decreased to less than 1 mg/kg ODW after 3 months of storage.

Conclusions

The following conclusions can be drawn about emissions from solid biofuels stored at the conditions used in this study:

● In sawdust, both dried and undried terpenes are emitted rapidly during the first 10 days. During this time there are no aldehyde emissions.
● As terpene emissions decrease, hexanal emissions increase. After 1.5 months, the hexanal in undried and dried sawdust peaks. In undried sawdust, the amount of

hexanal at its highest concentration is about equal to the remaining terpene content. In dried sawdust, the amount of hexanal at this time is about twice the amount of terpenes.
● For pellets, the emission of hexanal can be consistently higher than the emissions of terpenes. Hexanal emission reaches its maximum after about 1 month.
● Drying the sawdust does not affect the time for initiation and termination of fatty acid oxidation hexanal production.
● The wood is low emitting regarding both terpenes and hexanal after 2 months for undried sawdust, 2.5 months for dried sawdust, and about 3 months for pellets.

In general, differences between the tested materials were proven by keeping variables such as humidity and temperature as constant as possible during storage.

In pellet production plants, workers are exposed to emissions from undried and dried sawdust of various ages and from pellets. The results of this study clarify which substances are most likely to be a problem at various times. The domestic exposure from pellet storage would mostly be a problem for storage of pellets in which the wood is 2 to 3 months old. The contribution to ground-level ozone formation can be modeled by knowing the time frame of emissions of different volatiles. The risk of odors from wood pellets is likely to be highest about 1 month after drying. The risk of spontaneous ignition is greatest when relatively fresh pellets (1 to 6 weeks old) are stored in large silos.

The results indicate that although terpenes have been assumed to be the predominant volatiles emitted during the storage of sawdust and wood pellets, hexanal from fatty acid oxidation is also of importance.

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