Ann. occup. Hyg., Vol. 48, No. 4, pp. 339–349, 2004

Published by Oxford University Press
DOI: 10.1093/annhyg/meh015

Emission of Hexanal and Carbon Monoxide from Storage of Wood Pellets, a Potential Occupational and Domestic Health Hazard

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Received 23 June 2003; in final form 15 October 2003; published online on 10 March 2004

Objectives: The objective of the present study was to investigate and describe the emissions of volatile compounds, particularly hexanal and carbon monoxide, from large- and small-scale storage of wood pellets.

Methods: Air sampling was performed with Fourier transform infrared spectroscopy and adsorbent sampling in pellet warehouses, domestic storage rooms, lumber kiln dryers and experimental set-ups. Literature studies were included to describe the formation of hexanal and carbon monoxide and the toxicology of hexanal.

Results: A geometric mean aldehyde level of 111 ± 32 mg/m^3 was found in one warehouse, with a peak reading of 156 mg/m^3. A maximum aldehyde reading of 457 mg/m^3 was recorded at the surface of a pellet pile. Hexanal (70–80% w/w) and pentanal (10–15% w/w) dominated, but acetone (83 ± 24 mg/m^3), methanol (18 ± 7 mg/m^3) and carbon monoxide (56 ± 4 mg/m^3) were also found. The emissions in a domestic storage room varied with the ambient temperature and peaked after 2 months storage in the midst of the warm season. Aldehyde levels of 98 ± 4 mg/m^3 and carbon monoxide levels of 123 ± 10 mg/m^3 were recorded inside such storage rooms. Elevated levels of hexanal (0.084 mg/m^3) were recorded inside domestic housing and 6 mg/m^3 in a room adjacent to a poorly sealed storage area. Experimental laboratory studies confirmed the findings of the field studies. A field study of the emissions from industrial lumber drying also showed the formation of aldehydes and carbon monoxide.

Conclusions: High levels of hexanal and carbon monoxide were strongly associated with storage of wood pellets and may constitute an occupational and domestic health hazard. The results from lumber drying show that the emissions of hexanal and carbon monoxide are not limited to wood pellets but are caused by general degradation processes of wood, facilitated by drying at elevated temperature. Emission of carbon monoxide from wood materials at low temperatures (<100°C) has not previously been reported in the literature. We postulate that carbon monoxide is formed due to autoxidative degradation of fats and fatty acids. A toxicological literature survey showed that the available scientific information on hexanal is insufficient to determine the potential risks to health. However, the data presented in this paper seem sufficient to undertake preventive measures to reduce exposure to hexanal.

Keywords: air sampling; exposure; FTIR; work environment

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INTRODUCTION

The production of wood pellets is a relatively new industrial activity in Sweden. Wood pellets are increasingly used as a source of renewable energy for industrial, municipal and domestic heating. According to the Swedish Pellet Producers Association the annual production in Sweden increased from 90 000 tons in 1994 to 714 000 tons in 2001. The raw material for wood pellets in Scandinavia is primarily wooden by-products from the sawmill industry. The dominant timbers are the common Scandinavian conifers Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The unprocessed material is stored in the open. It is ground and dried to ~8% water content and without any other additives pressed to pellets. The raw material is handled in a closed process under negative air pressure until the pellets are pressed, after which it is handled in the open in the warehouses. The typical wood pellet is 6 or 8 mm in diameter and 10–12 mm long and shipped to customers in sacks or in bulk on trucks or cargo vessels.

Information about the potential health hazards associated with the production and handling of wood pellets is sparse in the scientific literature and the emissions and occupational exposures in the workers' zones of wood pellet manufacturing have not previously been described. A screening study was performed in a pellet factory, initiated by workers' complaints of odour and irritation of the eyes and respiratory system, particularly while working in the pellet warehouse (Svedberg and Galle, 2001). Hexanal, pentanal, methanol, acetone and carbon monoxide were identified by Fourier transform infrared (FTIR) spectroscopy and adsorbent sampling in the pellet warehouse. The closed production system minimized emissions inside the production plant.

The objective of the present study was to investigate and describe the presence and formation of volatile compounds, particularly hexanal and carbon monoxide, from storage of wood pellets. Supplementary monitoring of emissions from kiln drying of wood was performed to determine if the emissions were specific for wood pellet production or more general in nature. Experimental laboratory studies were carried out to confirm the results from the field studies. Literature surveys were made on the formation of hexanal and carbon monoxide and on the toxicology of hexanal.

MATERIALS AND METHODS

FTIR sampling

Air sampling was performed using FTIR technique. An FTIR instrument (MB100; Bomem, Quebec, Canada) was equipped with a mercury–cadmium–tellurium (MCT) detector with a 1 mm^2 detector area (Belov Technology, New Brunswick, NJ). The sample air was continuously pumped (4–30 l/min) through a Teflon tube (13 mm) into the analytical gas cell (5.7 l, variable path length, 0.75–20.25 m; Foxboro Inc.). During sampling in the field, a particle filter type P3 was installed at the sampling tube inlet to protect the tubing and the analytical cell from contamination. The spectral information generated by the FTIR instrument was stored in a computer and the succeeding spectral analysis was made at the end of the sampling sessions. One location was sampled by filling Tedlar sampling bags (SKC) with sample air, that was then evacuated into the FTIR gas cell.

Spectral information was collected in the 600–4000 cm^{-1} wavelength region with 1 cm^{-1} spectral resolution. Qualitative and quantitative analysis was performed using LabCalc software (Galactic Inc., Salem, NH). When the spectral information displayed stable baselines with no interference by unknown compounds in the regions of interest, a classical least squares (CLS) method was used for the quantitative analysis, analogous to our application described elsewhere (Svedberg and Galle, 2000). The CLS analysis was modified to fit each set of sample spectra embracing the choice of the wavelength region, inclusion or exclusion of compounds and baseline adjustment. When the CLS method did not work satisfactorily, a peak area proportionality comparison was used. Both methods required the use of pre-calibrated spectra that were either generated in the laboratory by injecting known aliquots into the analytical cell or obtained from commercial spectral databases (Infrared Analysis).

The limits of detection (LOD) were calculated as three times the peak-to-peak noise level in an absorbance spectrum at 258 scans created by ratioing two consecutive background spectra. The LOD obtained for the identified compounds are presented in Table 1. The actual LOD may be less, due to spectral noise, skewed baselines and interfering peaks. The IR signal in the 'fingerprint region' (600–1300 cm^{-1}) is too weak to resolve individual straight chain aldehydes at the concentrations found. The strong aldehyde peak at 2712 cm^{-1} has approximately equal absorption for

Table 1. Limits of detection (LOD) limits with the FTIR system for identified compounds

	IR frequency (cm^{-1})	LOD (mg/m^3)
Aldehydes	2680–2740	1
Formaldehyde	2775–2783	0.5
Formic acid	1061–1144	0.03
Acetone	1180–1250	0.15
Methanol	970–1096	0.15
Carbon monoxide	2109–2092	0.27

the dominant straight chain aldehydes found in this study and the FTIR results are therefore expressed as hexanal equivalents based on this peak. Formaldehyde has a characteristic spectrum and can be singled out from other aldehydes.

Adsorbent sampling and analysis

Pumped and diffusion sampling was performed using thermal desorption tubes with Tenax TA and Air Toxics™ adsorbents (Supelco) (200 mg, 60–80 mesh). All pumped sampling was carried out with SKC pumps (model 224-30) and a flow rate of 30 ml/min.

Thermal desorption was performed with an automatic thermal desorption system (ATD-400; Perkin-Elmer). The sample was desorbed from the adsorbent into a cold trap packed with ~10–20 mg of Tenax TA. After injection the cold trap was heated at a rate of 40°C/s to the specified temperature. An outlet split was used. The parameters for the ATD-systems were: desorption temperature 250°C, desorption time 5 min, purge time 1 min, cold trap low temperature –30°C, cold trap high temperature 300°C, cold trap time at high temperature 5 min, desorption flow rate 30 ml/min, inlet split 0 ml/min, outlet split 10 ml/ min.

Gas chromatographic separation using an Autosystem XL (Perkin-Elmer) was performed by the use of a high resolution capillary column (CP Wax 52CB, catalogue no. CP8073; Varian), 60 m × 0.32 mm, DF 1.2 µm. The temperature program was 60°C (0 min), 6°C/min to 250°C (5 min). Detection was performed with a TurboMass mass selective detector (Perkin-Elmer).

Data collection was done at full scan in the mass range 35–300 *m/e*. The calculations were done by use of both full scan areas and areas at specified *m/e* values, depending on which compound was to be determined. The analyses were performed by Chemik Lab AB, Sweden.

Sample locations

Industrial warehouses. Three industrial production plants (A, B and C) using different methods for drying the raw material were included in the study. Plant A used a direct drying method with flue gases from a pellet-fired hot gas generator (400–500°C); plant B used a direct drying method using flue gases from a nearby iron blast furnace (450°C); plant C used an indirect drying method with a heat exchanger where the sawdust did not come into contact with the drying gases (195°C). Air sampling was carried out in the pellet warehouses. In plants A and B the samples were collected on the service walkways suspended over the pellet piles. Below and along the walkways, conveyor belts distributed freshly produced pellets into oblong piles. In plant C the samples were collected on top of the pile in Tedlar sampling bags.

Domestic storage rooms. In Sweden, wood pellets are increasingly finding their way into domestic houses, replacing in particular oil as the principal source of energy for heating purposes. Many house owners have built or set aside separate rooms where 3–6 tons of wood pellets can be stored. The rooms are normally filled with pellets by means of compressed air from bulk loading trucks. The emissions from three household storage rooms were investigated. In one storage, after delivery of 5 tons of freshly produced pellets in a closed storage bin, the emissions and the temperature in the centre and above the pile were monitored continuously over 3 months. FTIR samples were collected in the air space (7 m^3) above the pellet pile. The air was circulated to the FTIR and back to the bin. The specific air exchange rate of the bin was calculated using a tracer gas (N_2O) decay method and FTIR for detection. A second continuous measurement lasted for 18 h after delivery of 6 tons of freshly produced pellets. This time the air was pumped from the bin to the gas cell and vented outdoors (30 l/min). The concentration due to leakage of emissions into the room adjacent to the storage bin was also determined. Emission leakage was further investigated inside two other houses adjacent to the in-house closed storage rooms. Sampling was performed by diffusion sampling on Tenax adsorbent over 10 days.

Laboratory tests. Emissions from wood pellets produced at the three production plants A, B and C were investigated in the laboratory. Pellets (10 kg) were placed in a galvanized steel canister, with a 1 cm air gap, on a thermostatically controlled hot plate. The canister had an air inlet in the bottom and an outlet at the top that was connected by Teflon tubing to the FTIR analytical cell and an air pump. The room air was thus pulled through the pellets and into the analytical cell. The flow rates were either 4 or 30 l/min depending on the application. Temperature sensors were positioned at the bottom and in the surface layer of the pellet bed. The thermostat was adjusted until a dynamic temperature at the bottom of the canister of ~80°C was achieved, producing a surface temperature of 35–40°C. To minimize the risk of condensation the analytical cell was heated to ~70°C and the canister and the connecting tubing were thermally insulated. Samples of the room air were used as reference spectra, thus reducing possible interference from background levels of carbon monoxide.

Kiln drying of lumber. The emissions from industrial kiln drying of Scots pine were investigated. The dryer was loaded with 115.5 m^3 of lumber (25 × 125 mm). The FTIR instrument was connected by 10 m of Teflon tubing to the exhaust duct of the kiln. The analytical cell was preheated to ~70°C. The

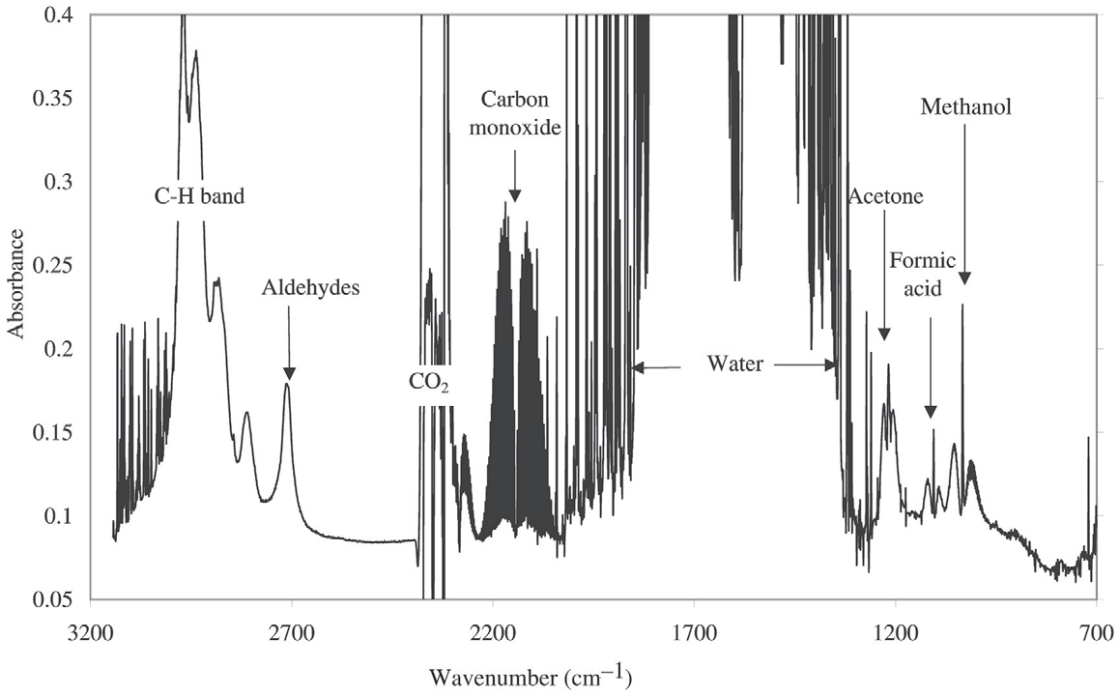

Fig. 1. An FTIR spectrum from the service walkway in plant A.

drying schedule was automatically regulated to control the rate of water removal. Initially the drying chamber was heated to 55°C before ventilation was started. The temperature was then slowly increased to a final value of 68°C. The total drying time was 95 h, during which the moisture content was reduced from ~50 to 10% (w/v).

RESULTS

Industrial warehouses

The FTIR measurements inside the warehouses at plants A (3 h) and B (18 h) showed that the dominant organic compounds were aldehydes (50–60% w/w), acetone (30–40% w/w) and methanol (10% w/w) (Fig. 1). A geometric mean aldehyde level of 111 ± 32 mg/m^3 was found in plant B on the service walkway, with a peak reading of 156 mg/m^3. Hexanal (70–80% w/w) and pentanal (10–15% w/w) predominated, but acetone (83 ± 24 mg/m^3), methanol (18 ± 7 mg/m^3) and carbon monoxide (56 ± 4 mg/m^3) were also found. A maximum aldehyde reading of 457 mg/m^3 was recorded with the sampling probe resting on the top of the pellet pile. The measurement was taken during a period with elevated pile surface temperature (0.2 m down the temperature was 88°C; 1.5 m down, 67°C; and 2.0 m down, 54°C.). A Tenax sample taken in parallel with the FTIR sample in Plant B showed the presence of the compounds indicated in Fig. 2, some of which are quantified and listed in Table 2. Formic acid was only found in plant A at a level of 1.6 ± 0.4 mg/m^3, while the levels of the other compounds were two to three times lower than in plant B. The warehouse at plant C had low pellet levels and an ambient temperature of –10°C during sampling. The measured concentrations were below the detection limit for FTIR except for carbon monoxide (0.8 mg/m^3).

Domestic storage rooms

The first measurement during 3 months inside a closed but passively ventilated storage bin showed that the emissions increased with the ambient temperature (Fig. 3). The mean aldehyde level was 21 ± 7 mg/m^3 and that of carbon monoxide was 21 ± 8 mg/m^3 (geometric means). The highest level, 49 mg/m^3, was recorded 2 months after delivery of the pellets. The second measurement during the initial 18 h after a new pellet delivery showed considerably higher levels of aldehyde (98 ± 4 mg/m^3) and carbon monoxide (123 ± 10 mg/m^3). The aldehyde level in the room adjacent to the storage bin reached 6 mg/m^3 during this period. The mean specific emissions of aldehydes for the two different loads of pellets were 96 and 703 mg/ton/day, respectively. The corresponding emissions for carbon monoxide were 100 and 885 mg/ton/day. The carbon monoxide levels correlated roughly with the aldehydes, but with a larger diurnal amplitude ($r^2 = 0.72$). Diffusion sampling on Tenax adsorbent inside two domestic houses

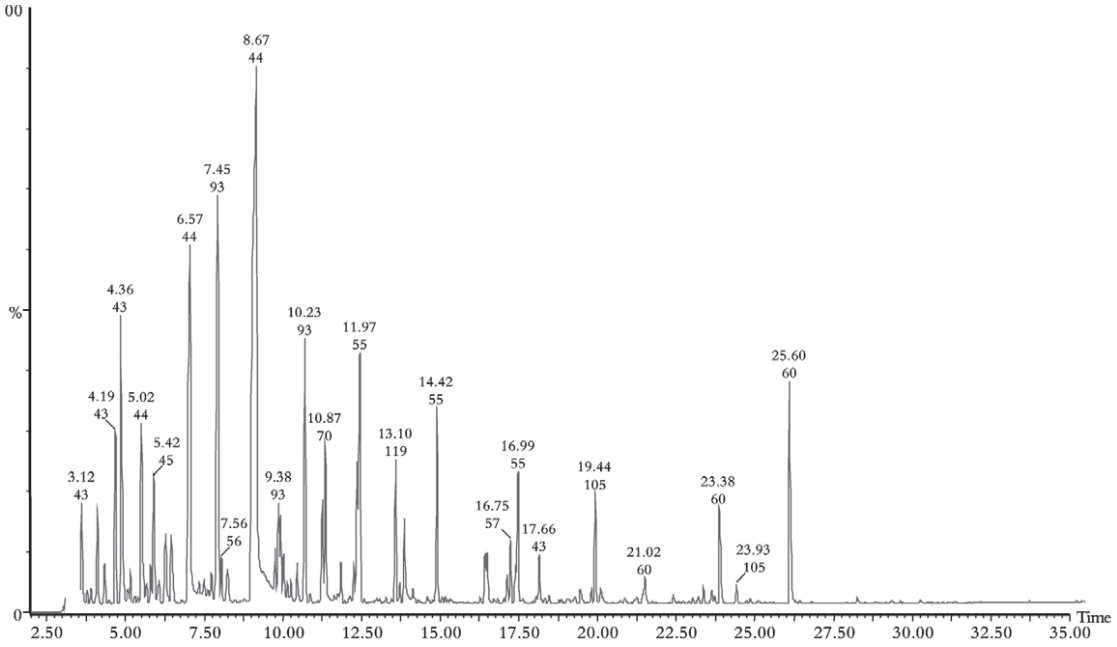

Fig. 2. GC-MS chromatogram from a Tenax sample also described in Table 2. The identified peaks with retention times are: 3.12, hydrocarbon; 4.19, acetone; 4.36, butanal; 5.02, isopropanol; 5.42, pentanal; 6.57, a-pinene; 7.45, *n*-hexanal; 8.67, b-pinene; 9.38, carene; 10.23, heptanal; 10.87, hydrocarbon (?); 11.97, methyl-isopropylbenzene; 13.10, octanal; 13.25, 2-heptenal; 14.42, nonanal; 16.00, 2-ethylhexanal; 16.99, benzaldehyde; 19.44, an acid; 21.02, pentanoic acid; 23.38, hexanoic acid; 25.60. Overloading of the sample is shown by the tailing of the peak for hexanal (8.67) and pentanal (6.57). This does not seriously affect the quantification according to laboratory sources.

Table 2. Sampling with Tenax adsorbent on a service walkway in plant A

	mg/m^3
Butanal	3.3
Pentanal	9.9
Hexanal	82.7
Heptanal	1.9
2-Heptenal	2.9
Nonanal	0.6
Decanal	n.d.
Terpenes	3.6
Toluene	0.36
n-Butanol	1.7

n.d., not detected.

adjacent to the closed pellet storage rooms showed raised levels of hexanal (0.056 and 0.084 mg/m^3), compared with zero levels in a reference sample outdoors.

Laboratory tests

The emission during an experiment with a 4 l/min air flow rate through the pellet bed is illustrated in Fig. 4. Aldehydes, methanol, acetone, monoterpenes, hexanoic acid and carbon monoxide were identified. The temperature at the bottom of the pellet bed was 40°C after 20 min, 50°C after 60 min and 60°C after 4 h. A steady temperature range of 72–75°C was reached after ~15 h. A flow rate of 30 l/min yielded 63% more total emissions after 130 h (5728 versus 3475 mg), compared with a flow rate of 4 l/min (Table 3). The total weight of the pellet bed decreased by 580 (30 l/min) and 502 g (4 l/min). The removal of water explains 99% of the weight loss.

Parallel sampling with Air Toxics, Tenax and FTIR for 8 min showed good agreement between the FTIR and Tenax samples, while the Air Toxics sample appeared to underestimate the concentrations (Table 4). Neither acetaldehyde nor its oxidized form acetic acid was detected.

Drying of lumber

The gradual formation of aldehydes and carbon monoxide during a complete drying cycle of lumber is described in Fig. 5. The levels were strongly correlated ($r^2 = 0.96$). The formation of other compounds like terpenes, methanol and ethanol were also detected, but are not described further.

DISCUSSION

Emission monitoring

Hexanal and carbon monoxide were found in the emissions from wood pellets and drying of lumber. The levels of carbon monoxide were at times above

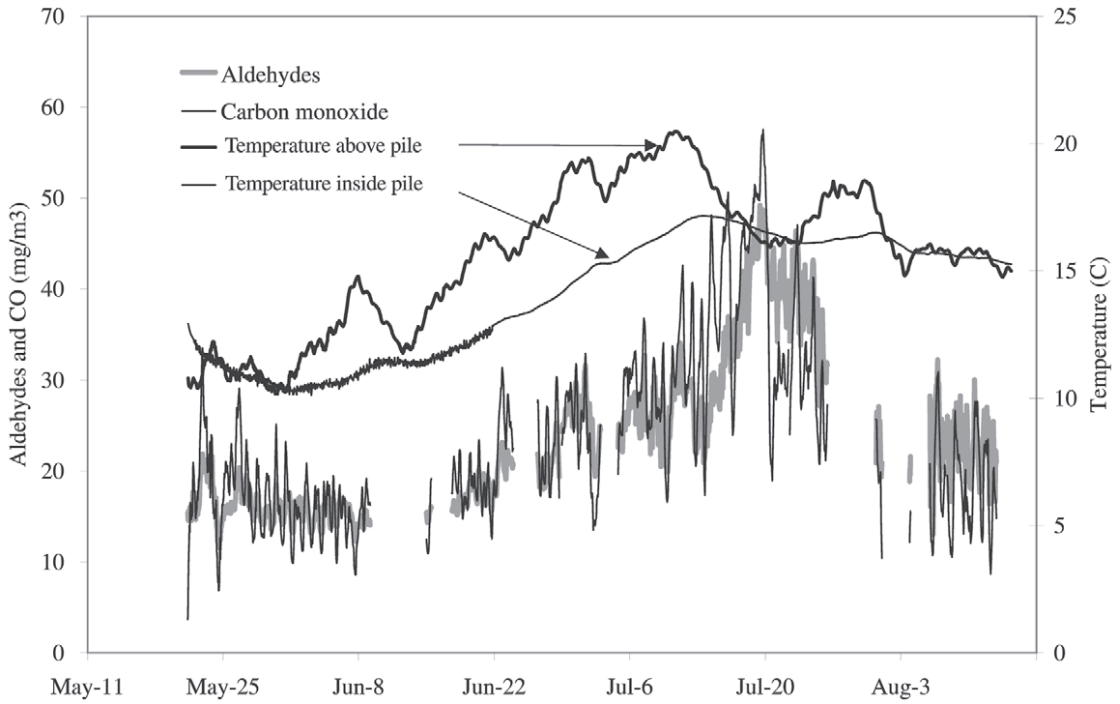

Fig. 3. Long-term FTIR measurement of aldehydes and carbon monoxide in a domestic storage room.

Table 3. Comparison of emissions in a flow-through experiment

	Emitted amount (mg)	
	4 l/min	30 l/min
Aldehydes	1739	1800
Hexanoic acid	406	2634
Acetone	422	294
Methanol	118	139
Carbon monoxide	705	820
Monoterpenes	85	41
Total	3476	5728

The samples are from the same batch where the 30 l/min sample was kept in a plastic bag at room temperature for 10 days. Aldehydes are expressed as hexanal equivalents.

Table 4. Parallel sampling during flow-through measurements

	FTIR (mg/m^3)	Tenax (mg/m^3)	Air Toxics (mg/m^3)
Butanal		n.d	1.3
Pentanal		16.3	8.3
Hexanal		48.1	4.9
Heptanal		1.7	0.4
Octanal		1.4	0.1
Nonanal		0.07	n.d
Decanal		0.02	n.d
Total aldehydes	66.6	67.6	15.0

the permissible occupational exposure level in the warehouses. The formation of hexanal and carbon monoxide in the experimental studies confirmed the findings of the field studies.

Pentanal, methanol, acetone and formic acid were identified and quantified by the FTIR method. Monoterpenes, other aldehydes and organic acids were found in substantially lower levels and required adsorbent sampling and GC-MS analysis for detection.

During the laboratory experiments the occasional occurrence of formaldehyde was observed at levels close to the detection limit of FTIR. Formaldehyde was not detected in the warehouses but it is likely that it would be detected using a more sensitive method. The absence of acetaldehyde in the results from the Air Toxics adsorbent samples indicate that high levels of acetaldehyde are not likely to occur in pellet warehouses. The laboratory experiments further showed no significant qualitative difference in the emissions from pellets produced by different drying methods.

Monoterpenes dominate the organic compounds emitted from fresh pine and spruce wood. However, both adsorbent sampling and FTIR results showed low monoterpene concentrations in the warehouses. The conclusion is that the greater part of the monoterpenes is emitted during the production of sawdust in the sawmills and the following storage, grinding and drying processes, before pressing of the pellets. A previous study has shown that the escape of

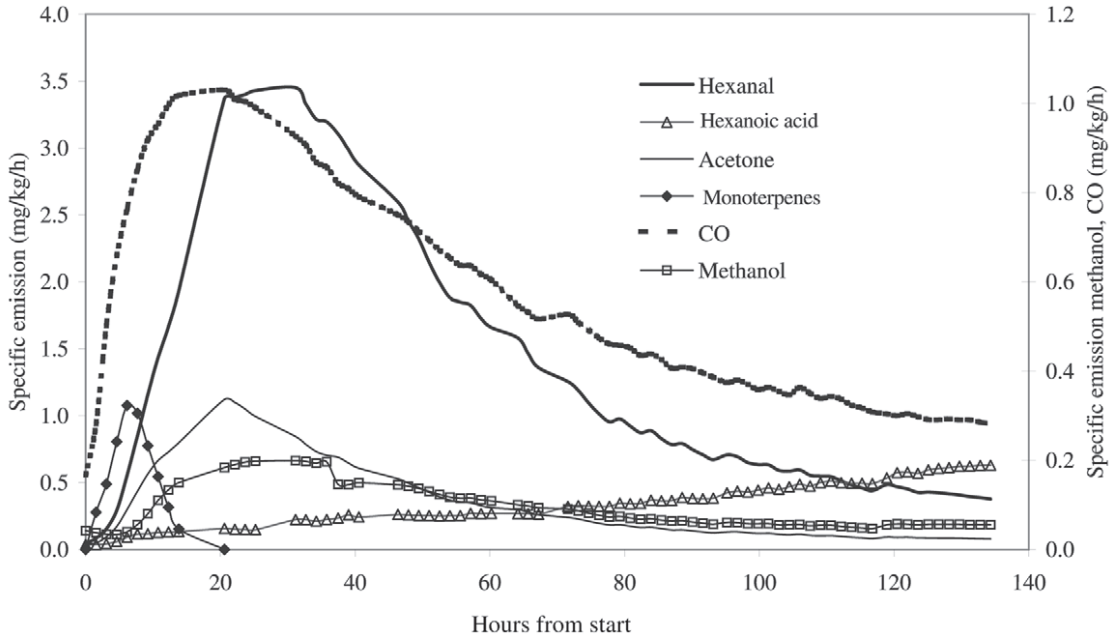

Fig. 4. Specific emissions from 10 kg pellets exposed to 4 l/min airflow.

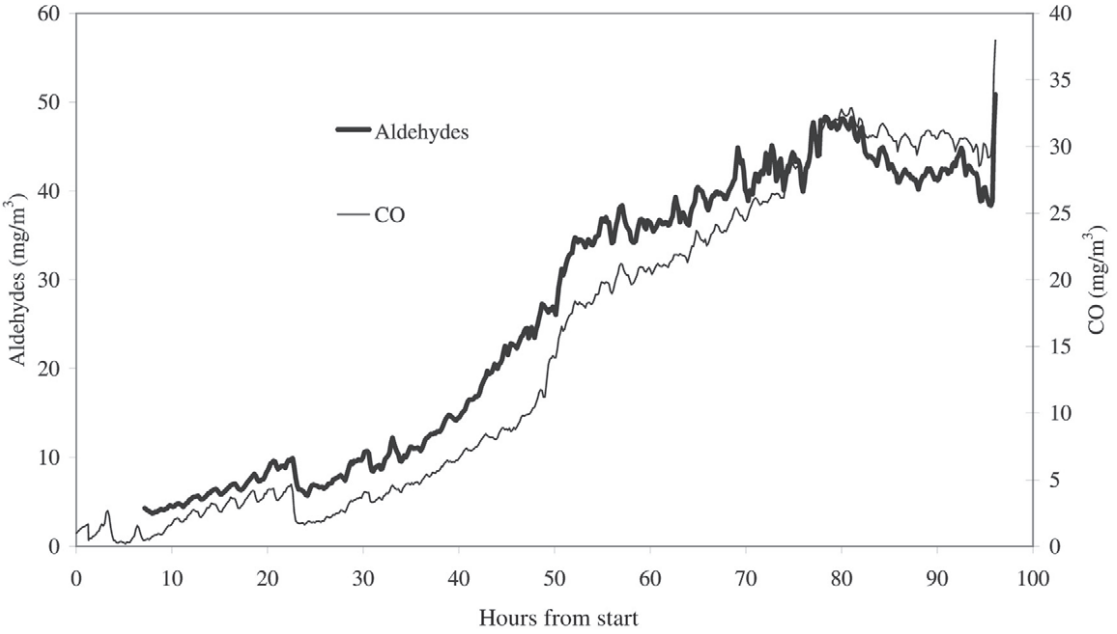

Fig. 5. The concentration of aldehyde and carbon monoxide in emissions from pine lumber drying.

terpenes from sawdust may be rapid (Risholm-Sundman *et al.*, 1998).

Considering the results from lumber drying it is concluded that the dominant emissions from wood pellets originate from general degradation processes in wood, which are initiated or facilitated by drying at elevated temperatures. When the processes take place in a confined space with large amounts of pellets, leading to a large surface area, the concentration of the emitted compounds may become high. From a working environment perspective the aldehyde levels in the warehouses may become too high. A maximum value of 457 mg/m^3 was recorded at the top of a pellet pile. It is not unlikely that operators may be exposed to such levels while working on the pile, for example, during leveling of the pile with graders and while

sampling temperature data. Carbon monoxide is well known to be toxic (Clayton and Clayton, 1982). The carbon monoxide levels were at times above the Swedish permissible exposure level of 40 mg/m^3 and it may be justified to install carbon monoxide alarms in warehouses and confined storage places which people enter. Formic acid levels sporadically reached 2 mg/m^3 in the warehouse, almost half the permissible exposure level in Sweden.

The laboratory tests with wood pellets identified the same group of compounds as found in the warehouses. The conclusion is that the drying process that takes place in the warehouses is well simulated by the experimental set-up used in the laboratory tests, although not driven to such an extreme. It was assumed that a limited upward air flow also exists inside the pellet piles in the warehouses. Heating of the laboratory sample aimed to resemble the conditions in the warehouse when elevated pile temperatures prevail. The total amount of aldehydes emitted was identical after 130 h, regardless of the flow rate. When all compounds were considered, the result was a higher total emission with the higher flow rate, which is principally explained by the increased emission of hexanoic acid, an oxidation product of hexanal. However, this was not accompanied by a corresponding decrease in the hexanal emission, which would be expected. The formation of degradation compounds may be limited by diffusion of oxygen into the wood structure analogous to what is described for other wood products (Back and Allen, 2000).

The conclusion is that the same compounds that were found in the warehouses caused the odour noticed by the end-user. The episodes with odour from the pellets seem to be more frequent during the winter months, based on informal discussions with end-users. The results show that the emissions vary greatly with different loads of pellets. A plausible explanation is that pellets that are produced, stored and distributed in the warm season have already emitted a large part of their volatile compounds in the warehouses. During the cold season the warehouse storage time of newly produced pellets is short and the emissions are released instead in the storage rooms of the end-users. A poorly designed storage room may cause leakage to the adjacent rooms and constitute a potential exposure risk, as demonstrated by the 6 mg/m^3 level measured outside a storage bin, accompanied by a strong odour. Measurements outside two closed domestic storage rooms, during a period when odour was not reported, indicated levels of hexanal of 0.056–0.085 mg/m^3, compared with 0–0.005 mg/m^3 normally found in the indoor environment (Brown *et al.*, 1994). The results show that the emissions from a domestic storage room can linger for several months and increase if the ambient temperature increases. If pellets are additionally vented or stored in the production step, it might reduce emissions in the storage rooms of end-users, however, storing at cold temperatures limits the release of emissions, as demonstrated in Fig. 3. Storage rooms should also be equipped with ventilation systems designed to prevent emissions from entering the living space.

The FTIR method is subject to calibration errors, spectral interference and sampling errors. The calibration error is estimated to be <5% and the error due to spectral interference <10%, but increasing when approaching the LOD. Condensation in sampling lines and leakage from line connections are potential sampling errors. Leakage was checked by periodic monitoring of the flow rate at the sampling tube inlet. Condensation of water was a problem in the kiln drying study. The condensate was therefore collected and analysed separately. The local variation in airborne concentrations in the pellet warehouses was probably the principal factor of measurement uncertainty. The measurements in the kiln dryer, the domestic storage room and in the experimental set-up were not affected by such variations. The present study further shows that the principal risk of relying on adsorbent sampling alone is that essential compounds in the investigated environments are simply not detected.

Formation of hexanal

Hexanal (CAS no. 66-25-1) was the predominant straight chain aldehyde found in the volatile organic compound mixture emitted from wood pellets. Apart from carbon monoxide, the volatile compounds identified in this report are previously known as low level emittants from wood and wood products and are often identified in indoor air investigations. Medium density fiberboard products (MDF) have been shown to emit hexanal for several months (Brown, 1999). The short chain aldehydes make up >50% of the volatile organic compounds which are emitted from MDF (Baumann *et al.*, 2000).

Hexanal and the other alkanals are probably formed by the oxidative degradation of natural lipids present in wood. The dry woods of Scots pine and Norway spruce contain 3–5% triglycerides and free fatty acids. A polyunsaturated acid, linoleic acid, is the major constituent in the mixture of free fatty acids and triglycerides found in such wood (Hoell and Piezconka, 1978; Piispanen and Saranpaa, 2002). Radical-induced oxidation by oxygen of linoleic acids or its esters yields hexanal as the major volatile component (Back and Allen, 2000). Such reactions can be either enzyme catalysed or occur through a so-called autoxidation process (Schieberle and Grosch, 1981; Frankel *et al.*, 1989; Noordermeer *et al.*, 2001). Because of the high temperature involved in pellet production, with enzyme denaturation as a probable consequence, the major path for this process in pellets most likely proceeds through autoxidation.

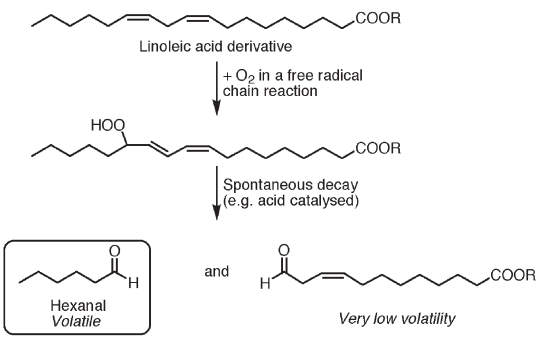

Fig. 6. Proposed pathway for the formation of the volatile aldehyde hexanal in wood pellets.

One possible route leading to hexanal is shown in Fig. 6.

Formation of carbon monoxide

The emission of one carbon compounds containing oxygen and hydrogen, such as methanol, formaldehyde and formic acid, from pellets is not surprising. The last two compounds may be autoxidation products of methanol. Other one carbon compounds are carbon monoxide and carbon dioxide. The high levels of carbon monoxide found in each of the measurements presented in this report were unexpected. It is well known that during the thermal anaerobic degradation of wood (pyrolysis) carbon monoxide emission occurs. The low temperature emission of carbon monoxide from wood products such as pellets has not been reported previously and the underlying chemical mechanism is uncertain. Carbon monoxide has a characteristic infrared spectrum and cannot be mistakenly identified. The possible interference of external sources of carbon monoxide was ruled out by the results obtained from laboratory tests with pellets produced by indirect drying (not exposed to drying gases containing carbon monoxide) and the results from the lumber dryer.

When various organic matters were stored at room temperature, particularly in the presence of air and light, small amounts of carbon monoxide were observed and the formation was enhanced by increased temperature (Levitt *et al.*, 1995). Microsomal lipids also produce carbon monoxide during peroxidation, initiated via different Fe(III) complexes. After initiation the reaction appears to be non-enzymatic, i.e. an autoxidative process (Wolff and Bidlack, 1976). Carbon monoxide (300–400 p.p.m.) has been observed in the air above 7000 tons of rapeseed stored in a sealed warehouse and the calculated specific emission rate has been estimated to be 200 mg/ton/day (Reuss and Pratt, 2001). Carbon monoxide has also been found in a wheat grain warehouse with a calculated specific emission rate of 9 mg/ton/day (Whittle *et al.*, 1994). These emission rates can be compared with the specific emission rates we found in the small pellet storage, ranging from 100 to 885 mg/ton/day.

The more rapid formation of carbon monoxide in materials with a high fat content (rapeseed) compared with those with a low fat content (wheat) indicates that carbon monoxide may be formed through the autoxidative degradation of fats. The measurements in this study indicate that the carbon monoxide and hexanal emissions are often correlated. We suggest that carbon monoxide formation during storage of the wood pellets is caused by the autoxidation of residual lipophilic extractives present in pellets, mainly fats and fatty acids. However, carbon monoxide formation from other organic materials present in wood, like cellulose, hemicellulose and lignin, cannot be ruled out.

Toxicology of hexanal

Hexanal was identified as a major component in emissions from wood pellets stored in industrial warehouses and under experimental conditions. Occupational exposure routes for aldehydes include inhalation and skin uptake. Food intake may also contribute to exposure (Feron *et al.*, 1991). Hexanal is rapidly metabolized in the body, the aldehyde being oxidized by aldehyde dehydrogenase to the corresponding acid (Marselos and Lindahl, 1988; Yoshino *et al.*, 1993; Fujita *et al.*, 1994; Townsend *et al.*, 2001). This seems to be the dominant metabolic route, but reduction of hexanal to the alcohol has also been suggested (Jaar *et al.*, 1999).

Low molecular weight aldehydes are strongly irritant to the mucous membranes in the nose, mouth and airways in humans (Clayton and Clayton, 1981). In eye irritation tests on rabbits hexanal was given grade 5 on a 10 grade scale (Grant, 1986). There are some reports concerning the genotoxicity of hexanal, however, most authors conclude that the risk to humans is negligible (Marinari *et al.*, 1984; Brambilla *et al.*, 1989; Martelli *et al.*, 1994).

Hexanal has cytotoxic potential in most cells tested but only in relatively high doses (Kaneko *et al.*, 1988; Martelli *et al.*, 1994; Muller *et al.*, 1996; Girona *et al.*, 2001). It should be noted, however, that *in vitro* studies suggest that insulin-producing cells in pancreas and sperm might be more sensitive than other cell types (Suarez-Pinzon *et al.*, 1996).

It is not possible to define a critical effect for hexanal. However, the high readings for hexanal and the relatively low readings for other emissions, as well as a general knowledge of the irritating effects of aldehydes, suggest that hexanal in the present settings can cause skin and mucous irritations and possibly also other health problems. As indicated in the Introduction, complaints about odour and irritation have been reported among exposed workers, but the frequency as compared with that in control groups is not known.

Conclusions

High levels of hexanal and carbon monoxide were strongly associated with storage of wood pellets and may constitute an occupational and domestic health hazard. The results from lumber drying show that the emissions of hexanal and carbon monoxide are not limited to wood pellets but are caused by general degradation processes of wood, facilitated by drying at elevated temperature. Emission of carbon monoxide from wood materials at low temperatures (<100°C) has not previously been reported in the literature. We postulate that carbon monoxide is formed due to autoxidative degradation of fats and fatty acids. The depletion of oxygen and simultaneous formation of carbon monoxide may be particularly dangerous in closed spaces.

A toxicological literature survey showed that the available scientific information on hexanal is insufficient to determine the potential risks to health. However, the data presented in this paper seem sufficient to undertake preventive measures to reduce exposure to hexanal both in the industrial environment as well in the domestic setting, where children and sensitive persons may be involuntarily exposed.

Acknowledgements—The study was financed by a grant from the Swedish Energy Agency and by Västernorrland County Council, Sweden. The authors would like to thank Christer Edling, Tony Waldron and Kåre Eriksson for valuable comments.

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