Section 1.9
Ref #31

PUBLICATION

GMR-4377R
ENV #153

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ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

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Volume18, Number 5
Pages 326–330

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■ Aldehyde emissions from wood-burning fireplaces were measured. Total aldehydes ranged from 0.6 to 2.3 g/kg of wood burned based on tests with cedar, jack pine, red oak, and ash. Formaldehyde, acetaldehyde, and *p*-tolualdehyde were the major aldehydes emitted with formaldehyde comprising 21–42% of the total. Aldehyde and particle emissions were inversely correlated with burn rate and may also be related to wood type. On the basis of our measurements, nationwide aldehyde emissions from residental wood burning were estimated to be between 14 and 54 Gg/year. This value is comparable to both power plant and automobile aldehyde emission sources. It is likely that residental wood burning is a major source of primary aldehydes during the winter.

Introduction

Aldehydes are emitted from a variety of sources, including power plants, automobiles, forest fires, and even natural vegetative processes (*1–3*). Aldehydes are also generated in the atmosphere by photochemical reactions of ozone and hydroxyl radicals with hydrocarbons. This secondary formation may be the major source of aldehydes in urban areas (*3*). Indoors, aldehydes are produced by combustion appliances, tobacco smoking, and outgassing of building materials.

At high concentrations, formaldehyde and many other aldehydes are irritants of the eyes, skin, and nasopharyngeal membranes. Formaldehyde is postulated to react with HCl in the atmosphere to produce bis(chloromethyl) ether, a suspected carcinogen (*3, 4*). Recent studies at the Chemical Institute of Toxicology indicated that formaldehyde can cause nasal cancer in rats exposed to high concentrations (15 ppm) of formaldehyde (*5*). Unsaturated aldehydes such as acrolein are also known to cause eye and respiratory tract damage (*3*). Other higher molecular weight aldehydes are less toxic than either formaldehyde or acrolein.

Another possible source of aldehyde emissions is residential wood combustion in fireplaces and wood stoves. In 1976, an estimated 28 million fireplaces and 7.6 million wood stoves were in use, and wood stoves are currently selling at the rate of 1.5 million a year (*6, 7*). Recent studies indicate that residential wood burning is presenting an air pollution problem in cities such as Vail and Denver, CO (*8, 9*).

Most of the previous studies on residential wood burning focused on particulate, polycyclic aromatic hydrocarbon, and CO emissions (*6, 10*). A few aldehyde measurements were made by DeAngelis et al. (*6*) on wood-burning fireplaces and stoves. They measured formaldehyde emissions of 0.4 g/kg and isobutyraldehyde emissions of 0.5 g/kg of wood burned. They found little difference with wood type or combustion equipment. In another study, Snowden et al. (*11*) reported emissions of 0.3–11 g/kg and 0.4–2.5 g/kg for formaldehyde and acetaldehyde, respectively. Due to the paucity of aldehyde data from residential wood burning, we initiated a study to characterize the aldehydes emitted from wood-burning fireplaces and to compare the results to aldehyde emissions from other sources.

Experimental Section

Test Procedure. Sampling was conducted on a Preway freestanding fireplace installed in the laboratory. The fireplace is a funnel-shaped steel structure, approximately 1-m diameter at the base. The exhaust gases were drawn by natural draft through a 20-cm diameter flue pipe to the roof. Four types of wood were tested: jack pine, cedar, red oak, and ash. A test consisted of burning a preweighed charge of dried wood to completion. Paper and matches were used to start the fire. The wood mass varied from 2 to 4 kg per test, and a test lasted between 25 and 77 min. Most of the tests were run with wood split into pieces of about 100 g each to faciliate a complete burn. However, quatered logs (logs of 1–2 kg each) were burned in two tests and any unburned wood was reweighed at the end of the test. Two tests were also made on a green ash wood with a moisture content of 20% compared to the other woods with moisture contents of less than 5%.

Particle Sampling. Particles were collected by using an EPA Method 5 sampling train (*12*). The sampling and

0013-936X/84/0918-0326$01.50/0

Table I. Fireplace Test Conditions and Emissions

wood	wood size	mass wood, kg	test time, min	average burn rate, k/min	average temp, °C	maximum temp, °C	particle emissions, g/kg	aldehyde emissions, g/kg	aldehyde/particle ratio
jack pine	split	4.1	30	0.14	183	413	5.6	0.952	0.17
cedar	split	2.0	37	0.05	106	321	12.7	2.260	0.18
red oak	split	3.5	31	0.11	181	265	6.9	0.951	0.14
red oak	split	4.1	36	0.11	182	468	6.6	0.917	0.14
red oak	split	4.3	26	0.17	237	513	4.5	0.611	0.14
red oak	quartered	2.4	40	0.06	178	262	12.9	1.075	0.08
green ash	split	2.9	33	0.09	153	322	4.6	0.937	0.20
green ash	quartered	2.4	77	0.03	71	187	19.8	1.862	0.09

temperature measurements were made from a port located 2 m above the grate. Stack gas was drawn through a 1.3-cm diameter nozzle and through a 1-m-long heated probe to a cyclone which removed large particles. The stack gas then passed through a heated filter and through two water-filled impingers which collected condensable organics. Three fractions were obtained: washings from the nozzle, probe, and cyclone with a 50% cutpoint at 10 μm; the filtered particles; the impinger catch. The front washings and impinger material were evaporated to dryness and weighed. The mass of the three fractions represents the particle mass. During the test, the temperature and air velocity were monitored every 3 min at the sampling point; the sample flow was adjusted accordingly to maintain isokinetic sampling conditions. More details on the characteristics of the emitted particle characteristics can be found in ref 10.

Aldehyde Sampling Procedure. Samples for aldehyde analysis were obtained from a 1.0-cm diameter port in the fireplace chimney, 2 m above the grate. The stack gas was drawn through a short Teflon line into two midget impingers containing 20 mL of a 2,4-dinitrophenylhydrazine solution in acetonitrile connected in series (*13*). The samples were drawn at a rate of 0.8 L/min by a pump, and the gas volumes were measured with a wet-test meter. In most cases, a single aldehyde sample was collected during the burn. In other cases, four samples were collected during various stages of the burn; one sample during the initial 2 min, two samples during the middle portion, and a final sample during the smolder stage of the burn. This was done in order to assess the aldehyde mass emission rate and distribution during various stages of the burn.

Aldehyde Analysis Procedure. Aldehyde emissions from the woods tested were measured by high-performance liquid chromatography using an improved 2,4-dinitrophenylhydrazine (DNPH) technique (*13*) developed in our laboratory. The method is based upon sample collection and in situ derivatization of the aldehydes and ketones in a midget impinger containing an acetonitrile solution of the reagent and catalyst. The resulting hydrazone derivatives are injected into a Varian-5020 liquid chromatograph for analysis.

The derivatives were separated on a 6-μm Zorbax ODS column (Du Pont Instruments). The mobile phase consisted of 67% acetonitrile/33% water, flowing at 0.7 mL/min for 8 min. The flow was then increased to 1.0 mL/min, and a linear gradient to 90% acetonitrile/10% water was generated over the next 17 min. Finally, the gradient was extended to 100% acetonitrile over the next 3 min.

Quantitation and identification were accomplished by external standards. Quantitation for unidentified peaks was based on the response factors for known aldehyde standards which eluted near the unknown peak. In our experience, response factors for closely eluting peaks are within 80–90% of one another.

Results and Discussion

The experimental conditions are listed in Table I with the total particle and aldehyde emissions for each test. The burn rate is the average rate during the test. Good agreement was obtained between emissions from the two red oak tests with similar burn rates. We found that the emissions varied inversely with the burn rate, with low burn rates yielding higher emissions. The tests with the lowest burn rate were the two tests with quartered logs and the test using cedar. Significantly higher particle and aldehyde emissions were measured during these tests. Conversely, the red oak test with the highest burn rate produced the lowest particle and aldehyde emissions. These results are in agreement with previous wood-burning results which showed that particle emissions are inversely correlated with burn rate (*10*).

The aldehyde emissions ranged from 8 to 20% of the particle emissions on a mass basis. In general, both particle emissions and aldehyde emissions increase or decrease together depending on the burning condition. However, the aldehyde mass emissions declined in relation to the particle mass during the slow burn rate encountered with the quartered logs. For instance, during the two ash tests, the particle emissions increased by a factor of 4 when the quartered logs were used whereas the aldehydes only increased by a factor of 2. There may be a relationship between wood type and emissions; cedar emitted twice the quantity of aldehydes as the red oak under similar burning conditions. However, there is not enough data in this limited sample to draw any conclusions. Also, the moisture content of the wood (green vs. dry) did not have a significant effect on aldehyde emissions.

Individual Aldehyde Emissions. Table II summarizes the individual aldehydes identified in the fireplace tests. The major aldehyde species found were formaldehyde, *p*-tolualdehyde, and acetaldehyde. Formaldehyde emissions ranged from 21 to 42% of the total aldehyde emissions (with the exception of one red oak test with only 8% formaldehyde). Also, *p*-tolualdehyde (10–26%) and acetaldehyde (7–14%) were major aldehydes emitted. Furfural and acrolein, two unsaturated aldehydes, and the ketone, acetone, were also present, with each species ranging from 1 to 13% of the total. Other aldehydes identified at the 1–3% level were crotonaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, valeraldehyde, and hexaldehyde.

The data also indicate that there are two groups of unidentified aldehydes or ketones in many of the fireplace runs. The first group of peaks have retention times that occur between butyraldehyde and benzaldehyde, while the

Table II. Fireplace Aldehyde Emissions, g/kg

aldehyde	jack[a] pine	cedar[a]	red[a] oak	red[a] oak	red[a] oak	red[b] oak	green[a] ash	green[b] ash
formaldehyde	0.356	0.550	0.315	0.326	0.237	0.089	0.389	0.708
acetaldehyde	0.105	0.200	0.093	0.083	0.086	0.148	0.086	0.136
furfural	0.061	0.072	0.030	0.056	0.031	0.035	0.072	0.225
acrolein	0.046	0.045	0.030	0.027	0.021	0.041	0.048	0.132
acetone	0.007	0.130	0.030	0.056	0.018	0.145	ND	0.007
propionaldehyde	0.015	0.040	0.017	0.012	0.009	0.088	0.020	0.014
crotonaldehyde	ND[c]	0.045	0.006	0.024	0.007	0.078	0.027	0.116
butyraldehyde	0.010	ND	0.9012	ND	ND	ND	ND	ND
unknowns	0.056	0.300	0.039	0.070	0.033	0.189	0.062	0.029
benzaldehyde	0.068	0.020	0.102	0.010	ND	0.003	0.010	0.002
valeraldehyde	ND	0.010	ND	ND	ND	0.003	ND	0.002
p-tolualdehyde	0.198	0.475	0.246	0.140	0.122	0.114	0.193	0.348
hexaldehyde	ND	0.075	ND	0.060	ND	ND	ND	0.027
unknowns	0.030	0.030	0.030	0.053	0.060	0.142	0.030	0.116
total	0.952	2.260	0.951	0.917	0.611	1.075	0.937	1.862

[a] Split wood. [b] Quartered logs. [c] ND means not detected, below the detection limit.

Table III. Aldehyde Generation Rate during Various Stages of the Burn, g/min

	green ash[a] at stage (time)[b]				red oak[a] at stage (time)			
	A (2 min)[b]	B (25 min)	C (32 min)	D (18 min)	A (2 min)	B (15 min)	C (15 min)	D (10 min)
formaldehyde	0.040	0.040	0.011	0.015	0.001	0.004	0.003	0.009
acetaldehyde	0.005	0.005	0.002	0.001	0.026	0.001	0.001	0.009
furfural	ND[c]	0.016	ND	0.001	0.016	ND	ND	ND
acrolein	0.015	0.001	ND	0.003	0.016	ND	ND	ND
acetone	0.005	ND	ND	ND	0.023	0.001	0.010	0.001
propionaldehyde	ND	ND	ND	0.002	0.050	0.001	ND	ND
crotonaldehyde	ND	0.005	0.002	0.005	0.023	0.009	ND	ND
p-tolualdehyde	0.017	0.018	0.005	0.011	0.051	0.011	ND	ND

[a] Quartered logs. [b] Sampling time for each stage given in parentheses. [c] ND means not detected, below detection limit.

second group of peaks have retention times greater than that for hexaldehyde. Although these compounds were not identified, the first group may be branched and olefinic C_4–C_8 aldehydes and ketones, while the second group may be higher molecular weight aromatic aldehydes and ketones. In any event, these higher molecular weight compounds were only present at about the 5% level.

Table III shows the aldehyde generation rate during various stages of the burn for two tests. Stage A represents the initial 2 min when the logs first catch fire. Stages B and C represent the period when flames are present. Stage D is the smolder stage after the flames have disappeared. The maximum temperature and, therefore, the maximum burning rate occur during stage B. Although the burn rate peaks in stage B, the generation rate is highest in stage A for red oak and comparable to the generation rate in stage B for green ash. These results indicate again that relatively high aldehyde emissions are emitted during the less-efficient initial burning conditions.

Source Comparison. The major sources of primary aldehyde emissions are aldehyde manufacturing operations, automobiles, power plants, and vegetative burning (*3*). Annual aldehyde emissions have been estimated for each source, as will be explained. In addition, we have used our fireplace emission values to estimate a residential wood-burning component. The annual nationwide emission estimates for each source are listed in Table IV.

Aldehyde Manufacturing and Power Plants. These emission values were taken directly from a National Academy of Sciences report (*3*). The data reported in Table IV are for 1979 fuel consumption in the U.S. of 480 Tg of coal, 5.2×10^8 barrels of oil, and 3.5×10^{12} ft^3 of natural gas (*3*). By use of these data, total aldehyde emissions from coal, oil, and gas power plants are about 23 Gg/year. This number may underestimate the power-plant contribution since only formaldehyde emission rates were reported, and the emission rates are at least 15 years old (*14*). Unfortunately, the lack of more recent power plant emission data limits this comparison.

Table IV. Estimated Annual Nationwide Emissions of Aldehydes from Various Sources

source[a]	emission rate	aldehyde emissions, Gg/year
wood burning	0.6–2.3 g/kg	14–54
aldehyde manufacturing		3
power plants		
coal	0.002 g/kg	1.0
oil	0.1 g/kg	8.0
natural gas	0.2 g/kg	13.5
automobiles[b]		
catalyst	0.020 g/mile	14
noncatalyst	0.130 g/mile	50
diesel	0.034 g/mile	0.4
vegetative burning[c]	0.003 g/kg	0.2

[a] This listing does not include all possible aldehyde sources. [b] These estimates are for automobiles only and does not include light- and heavy-duty trucks. [c] These values are highly speculative as detailed in the text.

Automobiles. The automobile values are based on emission measurements made at General Motors Research

(*15*). In 1981, approximately 64% of the vehicle miles traveled (VMT) were in catalyst cars, 35% in noncatalyst cars, and 1% in diesels. The total VMT for passenger cars was 1.1×10^{12} miles (*16*, *17*). The final aldehyde emission of 64×10^6 Gg/year can be compared to the NAS estimate of 120 Gg/year for all vehicles. The agreement is reasonable since they state that their value is only good to within a factor of 3.

Vegetative Burning. The acreage of land involved in burning was estimated to be 4.4×10^6 acres in wildfires and 3.0×10^6 acres in prescribed fires (*18*). Average "fuel" consumed is about 10 tons/acre for a forest fire and 4 tons/acre for a prescribed fire (*18*). Unfortunately, the only available emission value is 15 years old and indicates a formaldehyde emission of 0.006 lg/ton (3 mg/kg) (*19*). The emissions in Table IV are based on this emission rate. However, if we applied our emission rates to vegetative burning and assumed a 50% moisture content, the nationwide emissions would be 25 Gg/yr rather than the listed value of 0.2 Gg/yr. Obviously, there is a need for better emissions rate data.

Residential Wood Burning. We measured aldehyde emission rates from wood burning, which varied over a factor of 4, from 0.6 to 2.3 g/kg. Even greater uncertainty exists in the amount of wood burned. The most recent wood-burning assessment study used census values to determine the number of houses using wood as of 1976 (*7*). An average value for cords of wood burned per user was then assigned for each state. On the basis of these crude estimates, they determined that 27.9 million residences with fireplaces burned 2.7 Tg of wood, 912 thousand residences used wood stoves for primary heat and burned 5.1 Tg, and 7.6 million residences used stoves for auxiliary heat and burned 8.5 Tg of wood; a total of 16.3 Tg of wood. However, the most recent figures indicate that 13×10^6 stoves are currently in use (*20*). If the wood usage is proportional to that used in 1976, current wood usage in stoves should be 20.6 Tg. Under the assumption that fireplace usage has remained constant, the total wood use is presently 23.3 Tg. On the basis of our emissions measurements, nationwide annual aldehyde emissions from residential wood burning are estimated to be between 14 and 54 Gg/year.

We have used our emission values for fireplace and applied them to all residential wood burning based on the premise that the type of combustion equipment has no effect on aldehyde emissions. It is unclear if the lower burning rate or the higher temperatures occurring in stoves would increase or decrease the aldehyde emissions. Results from ref *6* and *21* indicate no definitive trend in either direction.

Of the sources considered in Table IV, the largest emissions are from noncatalyst cars, but this will be decreasing as the noncatalyst cars are phased out of the automotive pool. The aldehyde emissions from residential wood burning are comparable to power-plant emissions and within 22–84% of total automobile emissions. Unlike power-plant and automobile emissions, however, firewood usage is higher during certain times of the year and in certain geographical locations. Therefore, residential wood burning may be the major emission source of aldehydes in winter in areas where wood burning is popular.

Table IV deals only with primary sources of aldehyde emissions. As mentioned previously, secondary aldehydes are formed from hydrocarbon reactions in the atmosphere, and they may be the major source of aldehydes in urban areas. For instance, secondary aldehydes from vehicles in the U.S. were estimated to be about 4 times higher than direct emissions based on total hydrocarbons emitted (*3*). The same argument could be made for wood burning since the primary emission of about 1 g/kg aldehyde can be compared to volatile HC emissions of about 1.5 g/kg and condensable organic emissions of 4.5 g/kg (*10*).

Conclusions

Total aldehyde emissions from fireplaces ranged from 0.6 to 2.3 g/kg of wood burned based on several tests on cedar, jack pine, red oak, and green ash. Quartered logs were found to emit more aldehydes than the corresponding split logs, presumably because of the higher burn rate and combustion efficiency that is achieved with split logs. The aldehyde mass emissions averaged 14% of the particulate mass emissions. Formaldehyde, acetaldehyde, and *p*-tolualdehyde were the major aldehydes emitted with formaldehyde comprising about 21–42% of the total. Aldehyde and particle emissions were inversely correlated with burn rate and may also be related to wood type. However, no conclusions on aldehyde emissions from different wood types can be drawn from these limited tests.

On the basis of wood-burning emissions measurements and other source emission rates found in the literature, nationwide annual aldehyde emissions were estimated. Aldehyde emissions from residential wood burning were estimated to be between 14 and 54 Gg/year. This value is comparable to power-plant emissions and between 22 and 84% of all automobile emissions. It is likely that residential wood burning is the major source of primary aldehydes during the winter.

Acknowledgments

We thank Ken Kennedy for operating the fireplace testing facility and Margaret Leddy of Environmental Activities Staff for providing transportation statistics.

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Received for review May 25, 1983. Revised manuscript received November 16, 1983. Accepted November 30, 1983.