

Note: This is a reference cited in *AP 42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

Particulate and Gaseous Emissions from Wood-Burning Fireplaces

Jean Muhlbaler Dasch

General Motors Research Laboratories, Warren, Michigan 48090-9055

■ Particulate and gaseous emissions were measured from three wood-burning fireplaces. An average of 10 g of particles/kg of wood burned was emitted. The particles were spherical with a mass median diameter of about 0.17 μm . Although the material is carbonaceous, the organic carbon/elemental carbon split seems to depend on both the wood type and the size of the log burned. Benzo[*a*]pyrene emissions as well as Ames tests results on the particulate are reported. Continuous measurements of gases indicated average emissions of 110 g/kg CO, 1.5 g/kg HC, and 0.7 g/kg NO_x. The emission values measured here were used in conjunction with other measurements to estimate the importance of wood burning in wintertime Denver. Based on three estimating techniques, wood burning accounts for 20–30% of the Denver wintertime fine particulate.

Introduction

Wood burning has recently been recognized as an important particle-emission source in certain areas of the northern United States. For instance, as much as half of the respirable particulate in a residential area in Portland, OR, was attributable to wood burning (1). Recent wood-burning emission studies have centered on wood-burning stoves due to their rapid increase in recent years and the oxygen-deficit conditions under which they operate (2, 3).

Less attention has been paid to fireplaces since their use is not increasing as dramatically as wood stoves. However, fireplace emissions are still an important factor as evidenced by the fact that 58% of new homes built in 1976 had at least one fireplace (4). Fireplace use is still much more likely than wood-stove use in urban areas where pollutant levels are highest. In addition, a recent study of indoor air pollution from wood burning has shown higher levels of polycyclic aromatics from fireplaces compared to wood stoves (5).

A study of fireplace emissions has been completed by using two residential fireplaces and a freestanding fireplace installed in the laboratory. Measurements were made of gas and particle mass emission rates as well as the size and composition of the particles. On the basis of these findings and ambient measurements, the influence of wood burning on wintertime Denver particulate levels has been estimated.

Sampling Procedures

Over 40 fireplace tests were performed, both at residences and in the laboratory. Residential sampling was conducted at two homes, both of which had brick fireplaces built on an outside wall of the house. An aluminum chimney extension with an 8-cm port was placed on the

chimney, and the sample probe was inserted through the port. The two residences had chimney heights from 4.5 to 5 m above ground level.

Laboratory sampling was conducted on a Preway freestanding fireplace installed in the laboratory. The exhaust gases were drawn by natural draft through a 20-cm diameter flue pipe to the roof. The sampling port was located 2 m above the grate, and sampling equipment was positioned on scaffolding erected beside the fireplace. The burning rate was monitored by recording the change in mass of wood during burning. For this purpose, a weighing bucket rain gauge was modified to hold a wood grate rather than a rain bucket. The decrease in wood mass during combustion was recorded continuously.

Emissions from five softwoods and nine hardwoods were measured. In addition, two synthetic logs were tested, each consisting of a cellulose base held together with wax. A test consisted of burning a preweighed charge of wood that was split into pieces approximately 45 cm in length and 100 g each. Since it is impossible to simulate the vast variety of burning conditions used by homeowners, this standard condition was used to facilitate a fast, complete burn and to allow a comparison between wood types. For comparison, a few tests were also run with quarter or half logs. In these tests, the wood burned incompletely and was reweighed after a test.

Particles were collected by using standard EPA method 5 sampling procedures except that sampling was done from the center of the chimney rather than traversing the chimney. The temperature was measured at the sampling point. The sampling rate was adjusted every 3 min to maintain isokinetic sampling throughout the test. Three fractions of particles were collected, the front catch, the filter catch, and the condensable catch. The front catch consists of material that collects in the nozzle, probe, and cyclone. The cyclone collects particles greater than 10 μm in diameter. Beyond the cyclone is a Type A glass-fiber filter where the filterable material collects. The probe, cyclone, and filter are all held at 120 °C. Finally, the filtered gas stream passes through two water-filled impingers where the condensable material collects.

Particulate samples were also collected from diluted stack gas onto Nuclepore or Fluoropore filters. The exhaust was diluted three-to-one with filtered room air, thus allowing enough cooling for organics to condense. These samples were used for metal and SEM analysis.

Four gases, carbon monoxide, carbon dioxide, total hydrocarbons, and nitrogen oxides, were measured continuously during several laboratory tests. The monitoring instruments used were a Beckman-315A infrared analyzer for CO and CO₂, a Beckman-108A hydrocarbon analyzer,

and a Teco Model-10A chemiluminescent analyzer for nitrogen oxides.

Analytical Procedures

Mass. Particulate was collected on Whatman A glass-fiber filters. These were weighed before and after collection after equilibrating for 24 h at constant temperature and humidity. The front catch (nozzle, probe, and cyclone) was rinsed with deionized water and acetone into a pre-weighed beaker, taken to dryness over low heat, and re-weighed. The impinger water and rinsings, which made up the condensable catch, were treated similarly.

Particle Size and Morphology. A Sierra Series-220 stainless steel in-stack cascade impactor was used to obtain a size distribution of the particulate. Particles were collected on six stages on glass-fiber filter substrates that covered the range from less than 0.5 μm to more than 12 μm . The cascade impactor was allowed to reach stack temperatures before sampling began. The sampling rate was held constant during a test.

A TSI Model-3030 electrical aerosol analyzer (EAA) was used to obtain the particle size below 0.5 μm . Diluted exhaust was drawn through the EAA to obtain the size distribution from 0.01 to 1 μm . Since the particle loading was continually changing, the step 3 voltage was measured between each step voltage and used for normalization.

Carbon. All filters were analyzed for organic and elemental carbon by using a modification of the method of Cadle and Groblicki (6). The original method consisted of heating a 1-cm² section of filter to 650 °C in helium. Organics were volatilized and catalytically oxidized to CO₂. During the second stage of analysis, air entered the system, and the elemental carbon was oxidized to CO₂. The CO₂ levels from the two stages were related to the organic and elemental carbon concentrations, respectively. It was possible that some of the organic carbon charred in the first stage of analysis. Charred material was then detected as elemental carbon in the second stage. It was found that charring is a large problem for natural products such as wood. For this reason the method was modified in the following manner: One sample was run by using the original method. A second sample of each filter was heated in a tube furnace to 350 °C in air, which was hot enough to remove organics but was not hot enough to cause charring. After the organics were removed, the sample was then analyzed for elemental carbon by the original method. The difference between the total carbon determined by the first method and the elemental carbon determined by the second method represented the organic carbon. For illustration of the extent of the charring problem, the apparent elemental carbon content of the hardwood emissions decreased on the average from 41% to 5% after charring was eliminated by the modified procedure.

Percent Extractable and Benzo[a]pyrene. The extractable percentage and benzo[a]pyrene (BaP) concentrations were determined by the method of Swarin and Williams (7). A portion of the glass-fiber filter was extracted in benzene-ethanol and taken to dryness to determine the extractable fraction. The extract was then reextracted in hexane-methylene chloride, dried, and dissolved in acetonitrile. An aliquot was injected into a liquid chromatograph with a Zorbax ODS column, and the BaP was detected by fluorescence techniques. Since BaP may not be collected efficiently by a heated filter, extracts from impinger collections were also analyzed. No effort was made to determine the total collection efficiency for BaP using EPA method 5 collection techniques.

Ames Testing. A sample of the material extracted from the filter was taken to dryness and dissolved in dimethyl

Table I. Particulate Emissions from Wood-Burning Fireplaces (g/kg)

wood type	test location	no. of tests	emissions	
			av	range
softwoods				
Ponderosa Pine	residential	3	4.9	3.7-5.5
Pinyon Pine	residential	1	5.0	
Eastern Spruce	laboratory	3	13	10-15
Jack Pine	laboratory	4	10	6-14
Cedar	laboratory	1	13	
hardwoods				
Willow	residential	2	17	15-18
Americal Elm	residential	1	1.5	
White Ash	residential	3	7	2-15
Sugar Maple	residential	1	17	
Hickory	residential	2	2.9	2.1-3.7
Soft Maple	laboratory	2	9.3	9.0-9.6
Birch	laboratory	2	12	10-15
Hard Maple	laboratory	2	11	10-11
White Ash	laboratory	2	12	9-14
Red Oak	laboratory	7	8.8	6.6-12
synthetic logs				
type I	residential	1	5.9	
type I	laboratory	1	19	
type II	laboratory	1	20	

sulfoxide and sent to Litton Bionetics for Ames testing. Five doses of the sample (usually 10, 25, 50, 100, and 200 μg of extracted material) were added to the test system consisting of a *Salmonella typhimurium* strain in a growth medium. One set of these plates represented a nonactivated system and a second set was activated with S9 homogenate prepared from adult male rat liver. The plates were incubated for 2 days, and the number of revertant colonies were counted. A negative control consisting of the solvent alone and a positive control consisting of a compound known to revert the strain were run with all tests.

Potassium. Particulate was collected from a diluted stack gas stream onto Nuclepore or Fluoropore filters. After an acid digestion, potassium was measured by atomic absorption.

Results

Test Characteristics. The tests lasted from 15 to 206 min with the synthetic logs and halved logs taking the longer times. The median test time was 42 min. The average gas velocity during a test varied from 62 to 1330 fpm with a median velocity of 560 fpm. The average temperature at the sampling point during a test varied from 39 to 155 °C with a median of 88 °C. The maximum temperature recorded was 308 °C.

Particle Emissions. The particle emissions from 39 tests using either split wood or whole synthetic logs are shown in Table I. Total particle emissions varied from 2 to 18 g/kg with averages of 9 ± 4 g/kg from softwoods (12 tests), 10 ± 5 g/kg from hardwoods (24 tests), and 15 ± 8 g/kg from synthetic logs (3 tests).

The average fractionation of the particulate between the front catch (nozzle, probe, and cyclone), filter catch, and impinger catch is shown in Table II. The soft- and hardwoods are similar, with half of the material collected in the impingers and the other half divided between the front catch and filter catch. The synthetic logs show large variations between brands and even between tests with the same logs. However, in general, over half of the particulate emissions from the synthetic logs is collected on the filter.

The log size seems to have the greatest effect on particulate emissions. Most of the tests were run with split wood (pieces of wood about 100 g each) to facilitate a fast, complete burn. However, a few tests were run with halved

Table II. Fractionation of Particulate Collected

	no. of tests	front catch, %	filter catch, %	impinger catch, %
softwoods	11	32 ± 11	27 ± 13	41 ± 18
hardwoods	23	21 ± 12	26 ± 15	53 ± 19
synthetic woods	3	12 ± 5	59 ± 13	29 ± 16

Table III. Effect of Log Size on Particulate Emissions (g/kg)

wood	front	filter	impinger	total
Pinyon Pine (split)	1.4	1.9	1.7	5.0
Pinyon Pine (halved)	0.7	2.6	4.7	8.0
Soft Maple (split)	2.1	1.5	5.7	9.3
Soft Maple (quartered)	2.6	3.9	17	24
Red Oak (split)	2.7	2.9	3.9	9.5
Red Oak (halved)	3.3	3.6	22	29

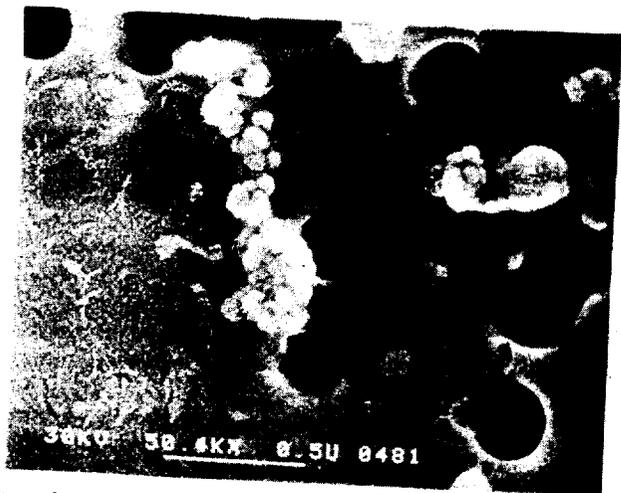


Figure 1. Scanning electron micrograph of wood-smoke particles on a Nuclepore filter. Line indicates length of 0.5 μm .

or quartered logs where each log weighed about a kilogram. This led to decreased burn rate, temperature, and flow rate. Since the logs burned only partially, they were reweighed after a test to obtain the mass emission rate. The results are shown in Table III. Total particle emissions are higher when large logs are used. This is due almost entirely to the impinger collection, which is the organic material. This may be due to insufficient oxygen or temperature for complete burning, leading to higher organic emissions.

Morphology. A representative scanning electron micrograph of the particulate from a red oak test is shown in Figure 1. The particles, which are on a 0.4- μm pore Nuclepore filter, consist of clusters of spheres. The particle size ranges from about 0.05 μm for a sphere to about 1 μm for a large cluster of spheres. The material looks similar to diesel exhaust particles (8).

Size Fractionation. Five cascade-impactor tests were made. Sampling lasted the entire time that flames were present and varied from 19 to 42 min for the five tests. In all cases, the majority of the material mass (83-90%) was on the backup filter. There were no obvious differences between softwoods, hardwoods, and synthetic logs. Since most of the particles were too small to be fractionated with the cascade impactor, the electrical aerosol analyzer was also used to obtain a size distribution below 1 μm . The resulting distribution is shown in Figure 2. The mass median diameter was approximately 0.17 μm .

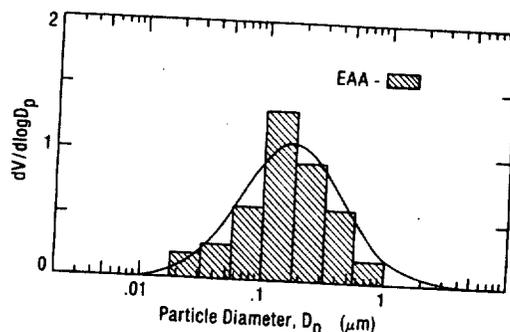


Figure 2. Size distribution of wood-smoke particles obtained with an electrical aerosol analyzer.

Table IV. Carbon Content of the Particulate

wood	no. of tests	organic carbon, %	elemental carbon, %	remainder, %
softwoods	7	38 ± 6	33 ± 13	29 ± 15
hardwoods	14	46 ± 7	8 ± 7	46 ± 7
synthetic	3	49 ± 2	15 ± 15	36 ± 4

Carbon Content. The carbon content of the emissions was measured in 21 tests. The front catch (probe and cyclone material) was assumed to be the same composition as the filter catch. The filter catch was analyzed by the carbon method described earlier. The impinger material was assumed to be entirely organic material. On average, it was 45% carbon, with the remainder consisting of organically bound oxygen and hydrogen.

Based on these three fractions, the carbon analyses of the total particulate from several tests are shown in Table IV. The hardwood emitted much more elemental carbon than the softwood, which emitted primarily organic material. The synthetic log emissions were extremely variable. The two tests with one brand showed high organics and low elemental carbon, but another brand of log showed just the reverse.

Although the particulate in all cases is primarily carbonaceous, there are distinct differences between emissions from different woods. This is illustrated by using the method of Cadle and Groblicki (6) in which the filtered sample is slowly heated in air and the evolution of CO_2 is monitored. Thermograms from four types of wood are shown in Figure 3.

The top thermogram is from the burning of red oak. The filtered particulate was distinctly brown rather than black, which is suggestive of a low elemental-carbon content. Most of the carbon evolves at low temperatures (less than 500 $^\circ\text{C}$), indicating organic carbon being burned off. The second thermogram is from a less dense hardwood (birch). In this case, the filter was black and a second peak representing elemental carbon is seen at a higher temperature. The softwood, pine (thermogram c), had a larger high-temperature peak, corresponding to the higher elemental-carbon content. The final thermogram is from a synthetic log filter, which has a peak coming off at extremely high temperatures. The peak most likely indicates elemental carbon, but possibly in a more highly ordered structure.

Benzo[a]pyrene. Several filters and two impinger samples were analyzed for benzo[a]pyrene (BaP), which is a suspected carcinogen. The results are shown in Table V. Obviously, the results cover a very wide range. Tests 1 and 3 were made on the same type of wood, and the emission rates were quite different. Two aliquots of impinger water extracts were also analyzed. One sample had

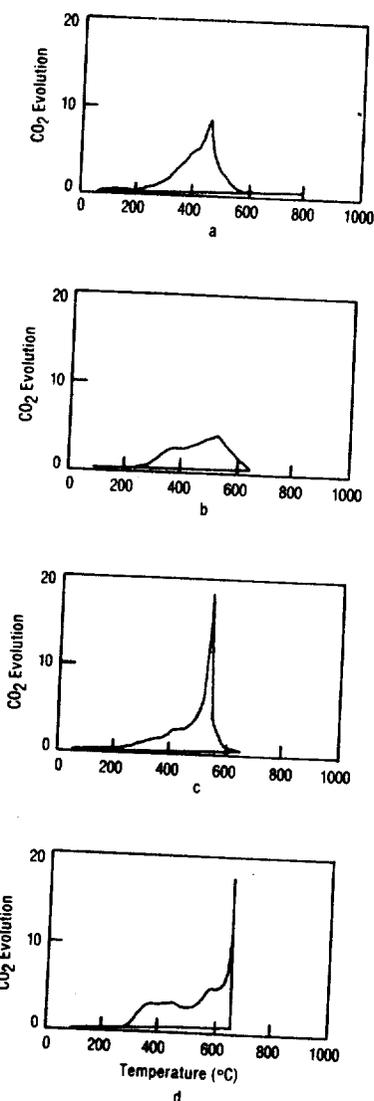


Figure 3. Thermograms from (a) red oak, (b) birch, (c) pine, and (d) synthetic log.

Table V. Benzo[a]pyrene Content of Filterable Fireplace Emissions

wood	ppm ^a	µg of BaP/kg of wood
Ponderosa Pine	24	50
Willow	105	700
Willow	141	1900
White Ash	3	5
White Ash	7	17
Sugar Maple	11	45
Hickory	120	130
synthetic log	18	58
synthetic log	40	400
average		370
median		58
coal, power plant ^b		2
coal, residential ^b		25000
auto, noncatalyst ^c		16
auto, catalyst ^c		0.4

^a µg of BaP/g of filterable particulate. ^b Reference 9. ^c Reference 10.

no detectable BaP, and the second sample (white ash) had a BaP content that corresponded to an emission rate of 0.08 µg/kg, an insignificant amount compared to the filter

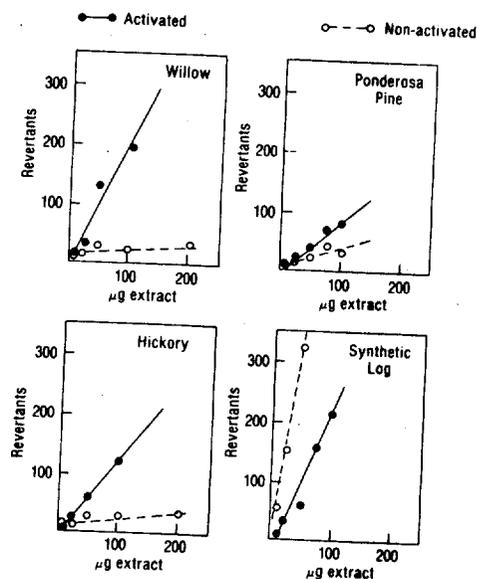


Figure 4. Results of Ames testing on four types of fireplace particulate extract.

catch levels. This suggests that the BaP is almost totally associated with the particulate emissions. For comparison, BaP emissions per kilogram of fuel are listed in Table V for other fuels. The only BaP levels that are higher appear to be those from less efficient combustion processes such as residential coal burning. In contrast, more efficient coal-burning in power plants produces much lower fuel specific BaP levels. Automobiles also emit some BaP, but most of this is destroyed by the catalytic converter.

Ames Tests. Since BaP levels in fireplace emissions are sometimes quite high, there also exists the possibility of mutagenic activity. Five extracted particulate samples were sent to a commercial laboratory for Ames testing. Graphs showing the revertants as a function of dosage for the sample extracts are shown in Figure 4 for both the nonactivated and activated samples. The control was subtracted from each sample. The slope of the graph in revertants/µg is a measure of the mutagenicity of the extracts. The slopes are shown in Table VI adjusted to the total amount of filtered material rather than just the extracted quantity. This makes a large difference especially for the synthetic wood, which showed high mutagenic activity but only 10% of the filtered particulate was extractable.

The three natural wood samples give similar results, with the nonactivated samples showing only minimal activity. At the highest dosage, the activity was approximately doubled over the control value. However, when activated with rat liver enzyme, all of these samples showed significant activity. The single impinger sample, which was extracted in dimethyl sulfoxide, showed very low overall activity but higher activity in the nonactivated test. The one synthetic log sample was interesting because it behaved differently from the natural woods. In contrast to the natural woods, the extract from the synthetic log burn showed lower mutagen activity when it was activated.

The natural wood emissions can be considered to be indirect-acting mutagens because activation was necessary to obtain a response. Chemicals such as benzo[a]pyrene and tobacco tar compounds are also indirect mutagens. There appears to be some correlation between BaP concentration and the activated dose response. However, it is unlikely that BaP itself is responsible for the activity since the detection threshold for BaP in an Ames test (200 ng/plate) is much higher than the doses used here (11).

Table VI. Results of Ames Tests

wood	extracted, %	nonactivated revertants, μg	activated revertants, μg	BaP, $\mu\text{g/g}$
Ponderosa Pine	46	0.14	0.38	24
Willow	74	0.067	1.5	105
Hickory	87	0.10	1.1	120
Hickory (impinger)	100	0.16	0.056	
synthetic log	10	0.67	0.24	40

Table VII. Gaseous Emissions from Fireplaces (g/kg)

wood	CO	HC	NO _x
softwoods			
Eastern Spruce	58	1.1	0.8
Jack Pine	160	1.1	0.2
hardwoods			
Soft Maple	120	2.7	0.8
Red Oak	90	1.6	0.8
Birch (dry)	71	1.0	
Birch (green)	180	1.4	0.7
synthetic logs			
Sterno	200	5.1	0.9
Northland II	120	9.7	1.0

The synthetic log emissions and possibly the impinger catch from natural logs are direct-acting mutagens in that activation is not necessary for a response. This is the type of behavior exhibited by nitro compounds and by extracts of vehicle exhaust particulates (11).

Potassium. The K/Fe ratio has been used to trace the contribution of wood smoke to ambient particle loadings (12, 13), based on the fact that wood emissions have a much higher K/Fe ratio than other combustion-source emissions. However, there is only one known measurement of these concentrations in wood smoke. Based on two tests of fireplaces burning softwoods, Watson measured concentrations of 5.3 mg/g K and 23 $\mu\text{g/g}$ Fe in the particulate (14).

We collected diluted wood smoke to analyze for K and Fe. Unfortunately, the iron concentration was so low compared to background that no reliable measurement could be made. However, as will be shown later, only the K concentration from woodsmoke is needed if the Fe level is as low as Watson's data indicated. The K concentration from three softwood samples was 4.1, 5.1, and 9.0 mg/g, and the concentration from three hardwood samples was 7.7, 10, and 13 mg/g. Although there is a large range of K concentrations within a wood type, the K levels from softwoods appear to be lower than from hardwoods.

Gases. Continuous gas measurements were made during eight tests, and the results are shown in Table VII. Average emissions for natural woods were 110 g/kg CO, 1.5 g/kg HC, and 0.7 g/kg NO_x. These values are similar to fireplace emissions estimates in AP-42 of 60 g/kg CO, 2.5 g/kg HC, and 0.5 g/kg NO_x (15). More recently, average values of 22 g/kg CO and 1.9 g/kg NO_x were measured by DeAngelis et al. (3). One explanation of the variability between studies is that the burning rate can greatly affect the emission of gases. For instance, the high burning rate employed in the latter study may have led to lower CO emissions and high NO_x emissions. Another problem is that the other studies based their results on grab samples rather than continuous measurements. Since gas concentrations vary by an order of magnitude during a test, it is important to make continuous measurements and integrate concentrations over the entire test time.

There are few obvious differences between the emissions for various wood types, although the synthetic logs appear to have higher hydrocarbon emissions. The green-birch

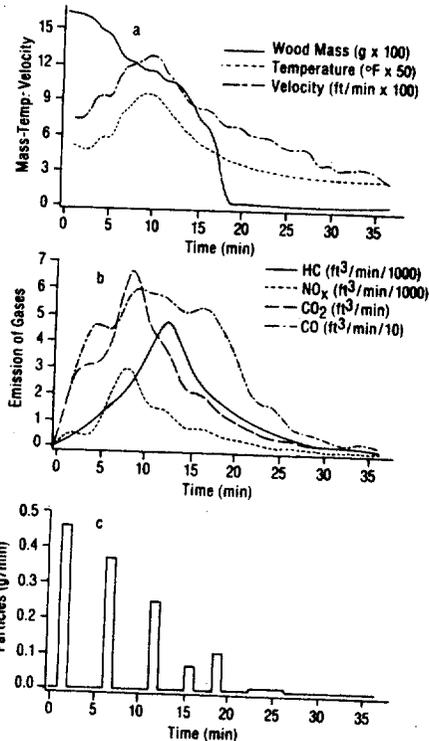


Figure 5. Continuous measurements during a birch burn of (a) burning parameters, (b) gas emissions, and (c) particle emissions.

burn led to higher CO and hydrocarbon emissions than the dried birch, probably due to the lower temperature of the burn.

Continuous measurements of wood-mass change, stack temperature, flow rate, and gas and particle emissions were made during several tests. The characteristic features of a natural wood burn are shown in Figure 5. The wood-mass change is only approximate since wood that fell off the grate was not measured. This occurred primarily at the end of a burn. The upper plot shows the decrease in wood mass during the burn and the temperature and velocity as measured 2 m above the grate. The velocity and the temperature track quite well. The center plot shows the continuous measurement of CO₂, CO, HC, and NO_x. The CO₂ and NO_x emissions peak at the same time as the temperature. Hydrocarbon emissions peak somewhat later. The CO emissions are much more erratic. The particle emissions, as shown in the lower curve, start high and decrease rapidly with time. This has also been shown by Butcher and Sorenson (2). It is interesting to note that gas and particle emissions continue after the flames have gone out. As much as 20-30% of the hydrocarbons and CO are emitted during this smolder stage. This is an important consideration when measuring emission rates of gases.

Discussion

The emission results measured here will be used to estimate the importance of wood burning in wintertime

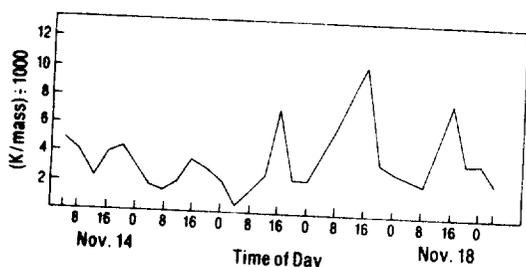


Figure 6. Daily variation in K/mass ratio in Denver ambient particulate.

Denver. Denver has a wintertime haze problem commonly referred to as the "Denver brown cloud". The cause of the visibility problem has been associated with fine particulate in the atmosphere. Two independent studies identified wood burning as responsible for part of the problem (12, 13). Based on ambient measurements made in Denver during the winter of 1978 by Countess et al. (16) and Wolff et al. (12) and the fireplace emission numbers measured here, it is possible to estimate the contribution of fine-particle wood smoke to the urban particulate problem. This will be done by using three different methods: (1) a mass emission estimate, (2) the K/Fe ratio method, and (3) the ^{14}C method.

Mass Emission Estimate. The importance of wood burning can be estimated by multiplying the mass of wood burned in Denver by the emission rate. The quantity of wood burned can be determined crudely, based on population. According to the latest housing census, there are 545 000 detached homes in the Denver Metropolitan Area. One report estimated that one-third of the houses in the country have fireplaces and that fireplace owners burn three-quarters of a cord of wood in a winter season (17). The fireplace season is assumed to be 150 days long. Therefore, the quantity of wood burned in Denver would be 1.0×10^6 kg/day. This compares favorably with an estimate of 1.2×10^6 kg/day burned in fireplaces in the Denver area based on a telephone survey (18).

Two common types of firewood used in Denver are ponderosa pine and pinyon pine. Samples of these two woods were shipped from Denver, and their emissions were measured. The total mass emissions (including impinger catch) ranged from 3.7 to 8.4 g/kg, averaging 6.0 g/kg. On the basis of two cascade-impactor measurements of softwood emissions, about 86% of the particles were in the fine-particle fraction of less than $2.5 \mu\text{m}$. This leads to fine-particle emissions from firewood of 5200 kg/day. Based on a source characterization in Denver, it can be estimated that fine-particle emissions from all sources are 17 000 kg/day (12). Therefore, fireplace emissions comprise 30% of the total emissions.

K/Fe Ratio. The ratio of K/Fe in the ambient particulate has been used as a tracer for firewood emissions (12, 13). Most sources have K/Fe ratios of 0.35 or less. Remote Colorado aerosol has a K/Fe of 0.38 (12). However, the K/Fe ratio from wood smoke is between 15 and 230 (14). Therefore, the ambient particulate K/Fe ratio will increase if wood smoke is a major source of air pollution. The two Denver studies have measured a diurnal variation in the ambient K/Fe ratio that peaks in the evening hours when fireplaces are most used. On the basis of ambient data collected by Wolff (19) in Denver in 1978, the ratio of K/mass has been plotted for 5 days in Figure 6. (There were too many missing Fe values to plot K/Fe.) There is clearly an increase in the K/mass ratio during each evening.

The wood-burning contribution can be determined based on the K concentration in wood smoke and average

Denver wintertime fine-particle concentrations by using the following formula:

$$K_D = K_w X + (K/Fe) F_{eD}$$

where K_D = average K concentration in Denver = $0.10 \mu\text{g}/\text{m}^3$ (16), K_w = K concentration in wood burning particulate, X = particle concentration due to wood burning in $\mu\text{g}/\text{m}^3$, K/Fe = background ratio = 0.38 (12), F_{eD} = average Fe concentration in Denver = $0.11 \mu\text{g}/\text{m}^3$ (16). The assumption is made that there is no wood-burning contribution to the Fe concentration. Since wood-particulate emissions contain about 23 ppm Fe compared to 3300 ppm in ambient particulate, this is a reasonable assumption (14). All of the concentrations used are for the fine-particle portion only. The K concentration from softwoods tested averaged 6.1 mg/g. From insertion of these values in the formula, the particle concentration due to wood burning (X) can be calculated to be $9.5 \mu\text{g}/\text{m}^3$. The average fine-particle mass is $33.7 \mu\text{g}/\text{m}^3$, so 28% of the wintertime Denver fine particulate is due to wood burning.

^{14}C Measurements. A final method for determining the importance of wood burning is based on ^{14}C measurements. Recently living material such as wood has a higher $^{14}\text{C}/^{12}\text{C}$ ratio than fossil fuels. By measuring the ^{14}C content of ambient particulate, it is possible to determine the fraction of "contemporary carbon" present. Since plant-derived material is insignificant in the winter and refuse burning is not permitted in Denver, the sole source of contemporary carbon is considered to be wood burning. The particulate carbon mass in Denver consisted of 33% contemporary carbon (12). Since 39% of the ambient fine particulate in Denver was carbon (16), 13% of the particulate was due to wood smoke carbon ($39\% \times 0.33$). The Denver wood particulate was analyzed for carbon content and was found to average 64% carbon. Therefore, the contribution of wood burning to fine-particle mass in Denver is 20% based on the ^{14}C technique.

Summary. The results of the three approaches were quite similar, considering the number of assumptions incorporated in each estimate. The fraction of fine particulate due to wood burning is 30% based on the amount of wood burned, 28% based on the K/Fe ratio, and 20% based on ^{14}C measurements. Therefore, it appears clear that wood burning has a significant effect on ambient wintertime particulate concentrations in Denver. Although these results cannot be generalized, wood burning may be an important source of atmosphere particulate in many locations.

Acknowledgments

I wish to thank Ken Kennedy and Stan Anderson for help with sampling, Steve Cadle, Pete Groblicki, Ron Williams, George Wolff, Tom Gibson, and Steve Swarin for helpful discussions, and Dave Stroup, Alice Ricci, Noel Potter, Walt Lange, Dave McEwen, Ed White, and Mark Myers for careful analytical work.

Literature Cited

- (1) Cooper, John A.; Currie, Lloyd A.; Klouda, George A., presented at the 73rd Annual Meeting of Air Pollution Control Association, Montreal, 1980.
- (2) Butcher, S. S.; Sorenson, E. M. *J. Air Pollut. Control Assoc.* 1979, 29, 724-728.
- (3) DeAngelis, D. G.; Ruffin, D. S.; Reznick, R. B. "Preliminary Characterization of Emissions from Wood-Fired Residential Combustion Equipment"; Monsanto, Dayton, OH, 1980, EPA-600/7-80-040.
- (4) DeAngelis, D. G.; Ruffin, D. S.; Peters, J. A.; Reznick, R. B. "Source Assessment: Residential Combustion of Wood";

- Monsanto, Dayton, OH, 1980, EPA-600/2-80-042b.
- (5) Benton, G.; Miller, D. P.; Reimold, M.; Sisson, R., presented at the 1981 International Conference on Residential Solid Fuels, Portland, OR, 1981.
 - (6) Cadle, S. H.; Groblicki, P. J., presented at the International Symposium on Particulate Carbon: Atmospheric Life Cycle, Warren, MI, 1980.
 - (7) Swarin, S. J.; Williams, R. L., presented at the 4th International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, 1979.
 - (8) McCrone, W. C., Ed., "The Particle Atlas"; 2nd ed.; Ann Arbor Science: Ann Arbor, MI, 1980.
 - (9) Nagda, N. L.; Pelton, D. J.; Swift, J. L., presented at the 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, OH, 1979.
 - (10) Williams, R. L.; Swarin, S. J., presented at the Society of Automotive Engineers Meeting, Detroit, MI, 1979.
 - (11) Wei, E. T.; Wang, Y. Y.; Rappaport, S. M. *J. Air Pollut. Control Assoc.* 1980, 30, 267-271.
 - (12) Wolff, G. T.; Countess, R. J.; Groblicki, P. J.; Ferman, M. A.; Cadle, S. H.; Muhlbaier, J. L. *Atmos. Environ.* 1981, 15, 2485-2502.
 - (13) Courtney, W. J.; Tesch, J. W.; Stevens, R. K.; Dzubay, T. G., presented at the 73rd Annual Meeting Air Pollution Control Association, Montreal, 1980.
 - (14) Watson, J. G., Ph.D. Thesis, Oregon Graduate Center, Beaverton, OR, 1979.
 - (15) U.S. Environmental Protection Agency, "Compilation of Air Pollutant Emission Factors", 3rd ed.; U.S. EPA AP-42, 1977.
 - (16) Countess, R. J.; Wolff, G. T.; Cadle, S. H. *J. Air Pollut. Control Assoc.* 1980, 30, 1194-1200.
 - (17) Stanford Research Institute "America's Demand for Wood 1929-1975"; Tacoma, WA, 1954.
 - (18) Ryan, P., personal communication.
 - (19) Wolff, G. T., personal communication.

Received for review November 9, 1981. Revised manuscript received April 22, 1982. Accepted May 17, 1982.

Vapor Pressure Correlations for Low-Volatility Environmental Chemicals

Donald Mackay,* Alice Bobra, Donald W. Chan, and Wan Ying Shlu

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A4

■ Four equations are proposed and tested that relate vapor pressures at ambient temperatures for low-volatility solid and liquid chemicals of environmental interest to their boiling and melting points. The equations may be used to estimate vapor pressure from boiling point, check the reasonableness of experimental data, or correlate these data. The preferred equation, which is a version of the Rankine equation, gives a mean error in vapor pressure of a factor of 1.25 for 72 selected hydrocarbons and halogenated hydrocarbons. It is suggested that versions of the equation may be developed for other classes of compounds.

Introduction

The tendency for an environmental contaminant or pesticide to partition into the atmosphere is determined largely by its vapor pressure. It is thus recognized that for assessing the likely environmental behavior of new and existing chemicals a knowledge of their vapor pressures is essential.

The vapor pressure P (Pa) can be regarded as a measurement of the maximum achievable amount or solubility of the substance in the vapor of air phase, the corresponding concentration being obtained from the gas law as P/RT (mol/m^3) where R is the gas constant (8.314 J/mol K) and T is absolute temperature (K). It is not always recognized that high molecular weight hydrophobic substances such as DDT or PCBs, which have very low vapor pressures and hence low atmospheric concentrations, may still partition appreciably into the atmosphere as they also have low aqueous solubilities. The ratio of the concentration in the atmosphere to that in the water (i.e., the air-water partition coefficient) may thus be large despite the low vapor pressure. This partition coefficient can be expressed as a dimensionless Henry's law constant H/RT where H is defined as the ratio of partial pressure P to aqueous concentration (mol/m^3). Compounds of high H tend to partition predominantly into the atmosphere, and the rate at which they evaporate from water is usually controlled by the water-phase mass-transport resistance. For substances of low H , partitioning is predominantly into

the water, and the evaporation rate tends to be controlled by the resistance in the air phase, where the concentration is lower.

It is noteworthy that many of the data published in the literature for vapor pressures are erroneous, especially for very low vapor pressure substances (Spencer et al. (1)). Little difficulty is encountered experimentally in measuring vapor pressures exceeding 1 kPa, since an isoteniscope can be used. For lower vapor pressures, the preferred approach is to flow a stream of gas through a vessel containing the volatile solid or liquid solute coated on packing, such that the gas stream is saturated. The exit gas is then analyzed for solute concentration. Such methods have been described by Spencer et al. (1), Sinke (2), and Macknick and Prausnitz (3), and although straightforward, they require meticulous experimental technique. For some substances of environmental interest the only vapor pressure information that may be available is the boiling point, and it is useful to devise methods of using these data to estimate vapor pressures approximately at lower temperatures. In this paper we thus examine the physical-chemical factors that influence vapor pressure, suggest correlations for fitting vapor pressure data, for determining vapor pressure from boiling point in the absence of experimental vapor-pressure data, and for checking the reasonableness of experimental vapor pressure data. Our focus here is thus on low vapor pressure solids or liquids well below their boiling point. For more volatile compounds, direct vapor pressure measurement is easy and there is little merit in prediction.

Thermodynamic Basis

A comprehensive discussion of the theory underlying liquid vapor pressure is provided by Reid et al. (4), and only the salient points are reviewed here. Typical vapor pressure characteristics of a substance are illustrated in Figure 1a. The range of environmental temperatures may lie anywhere on this diagram for a given substance, relative to the phase transition points. The solid and liquid vapor pressure lines are highly nonlinear, and no method is currently available for calculating from theory the mag-