Effect of Airflow Setting on the Organic Composition of Woodheater Emissions

TIMOTHY B. JORDAN* AND
ANDREW J. SEEN

School of Chemistry, University of Tasmania, Locked Bag 1371, Launceston, Tasmania, 7250, Australia

Fine particle emissions from woodheaters are large contributors to ambient atmospheric pollution in a number of regional centers in Australia. The health impact of woodsmoke is not limited to the particle loading alone, and a wide range of toxic inorganic and organic compounds are also emitted as gases or adsorbed onto particles. The organic composition of woodsmoke was determined from two heater models operated using different airflow settings. Particle emission factors varied between 3 and 36 g per kg dry wood burned, with higher burn rates (open airflow) producing significantly less particle mass per kg wood burned than the low burn rates (closed airflow). Over 90 organic compounds were quantified from the vapor- and particle-phases, including furans, methoxyphenols, and other substituted aromatics, PAHs, maltols, and the sugar levoglucosan. Emission factors for the majority of the particle-phase compounds increased as the airflow was progressively closed, but decreased for some PAHs and other compounds found predominantly in the vapor-phase. Levoglucosan was the single most abundant compound, contributing 5−16% of the total particle mass. Although there was some variation in levoglucosan emissions between heater models, the fact that levoglucosan emissions vary relatively little between airflow conditions for a given heater provides the potential to use it as a general tracer for woodsmoke. In contrast, the mass fractions of many other particle-phase compounds were considerably higher when operated with a closed airflow.

Introduction

With the introduction in Australia of the National Environmental Pollution Measure (NEPM) for Ambient Air Quality in 1998 (*1*), and concerns about documented health effects of airborne particulate matter (*2*), there is a need to apportion ambient air pollution to its sources so that regulatory bodies can deal accordingly.

The city of Launceston (population ∼80 000), located in the north of Tasmania, Australia, experiences severe pollution episodes during the winter. Episodes with PM_{10} levels greater than the 50 $\mu g/m^3$ guideline (24-hour average) stated in the Air NEPM occur 20−40 times per year, with maximum levels as high as 80−130 $\mu g/m^3$ recorded in the past few years. Wood burning, and slow-combustion woodheaters (woodstoves) in particular, are perceived as the main contributors. Around 46% of households used woodheaters or open

fireplaces in 2000, consuming a total of 66 300 t of firewood (*3*). In an effort to reduce the wintertime pollution, a "buyback" scheme was operated for nearly three years, in which households received a rebate for exchanging woodheaters for other forms of heating.

A technique used to determine relative contributions of pollution sources is a chemical mass balance (CMB) receptor model. This technique models the chemical composition of the ambient air as the linear combination of each compound emitted from each source multiplied by the sources' respective contributing factor. A comprehensive discussion and review of the application of CMB models is given elsewhere (*4*). The CMB method relies (in part) on all sources in an airshed having their emissions characterized, and that there are sufficient differences in the source profiles. Many organic compounds are present in woodsmoke, with suggested tracers consisting of methoxyphenols (*5*), potassium (*6*), levoglucosan (*7*), retene (*8*), and resin acids (*9*). For their use in CMB models, source profiles must be matched spatially and temporally to the area of interest. Thus, it is important to use locally available wood species and imitate local practices when undertaking source characterization studies. Extensive analysis of the organic and elemental composition of woodsmoke from woodstoves and open fires has been undertaken in the United States (*10−13*), but there remains a deficiency in source profiles from other areas of the world.

Previous studies have used emissions from open fires to apportion woodsmoke to ambient PM_{10} in a number of U.S. cities (*14−16*). Traditionally, a composite "wood burning" source profile is used in CMB models; however, separation of the contribution from hardwood and softwood combustion has been achieved recently by identifying compounds for which concentrations differed significantly enough to allow the CMB to differentiate the two source profiles (*13*, *15*).

Differences in emission profiles have been observed when burning different species of wood (*17*, *18*), and when using different types of appliances (*19*). Woodheaters operated with sufficient airflow (i.e., allowing "complete" combustion) produce significantly less particulate matter than when operated under "incomplete" or smoldering conditions (*20*). The affect of the operating conditions (burn rate) on the emission of organic species has not been fully characterized, though polycyclic aromatic hydrocarbon (PAH) emissions were found to be higher when burning Australian woods in woodheaters operated with a restricted airflow (*21*).

The objective of this study was to characterize the emission rates of various organic compounds under different combustion conditions to examine their potential for use in source apportionment studies. A number of source tests were conducted using two different woodheater models operated using a variety of airflow conditions, with over 90 organic compounds quantified in the vapor and particle phases. It is hypothesized that lower emissions of particle-bound organics are produced per gram of particle from woodheaters operated with a high airflow due to increased firebox temperature and oxygen availability.

Experimental Methods

Source Tests. A dilution tunnel (Figure 1) was built at the University of Tasmania and operated according to local Australian standards (*22*, *23*). The principle of this setup is to draw the entire woodheater flue emissions into a much larger volume of ambient air to cool it closer to "real world" conditions, allowing semi-volatile compounds to condense and thus be collected in the particle phase.

* Corresponding author e-mail: tjordan@utas.edu.au; phone: +61 3 6324 3830; fax: +61 3 6324 3839.
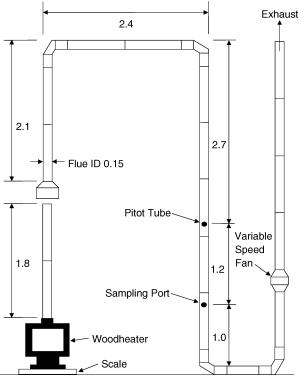
FIGURE 1. Woodheater dilution tunnel setup (dimensions are in meters).

Two different models of woodheater from the same local manufacturer were tested: heater S1 was approximately 15–20 years old, while heater S2 was a larger and much more modern design (about 5 years old) incorporating a secondary air inlet between the baffle and flue outlet. Both models had adjustable air inlets which allow restriction of airflow to slow combustion. The dimensions of the heaters were 54 × 42 × 40 cm and 62 × 50 × 46 cm (width × height × depth) for S1 and S2, respectively.

The firewood used in all the tests, White Gum (*Eucalyptus viminalis)*, was obtained from a local wood merchant. Although many households collect their own firewood, obtaining wood from a merchant was aimed at representing a typical species of locally available wood. The average moisture content of the wood on a dry basis was $13.8 \pm 0.9\%$ w/w ($n = 6$), determined by drying portions of wood (30–200 g) at 105 °C until constant weight was obtained.

Each source test was started by using a few sheets of newspaper and kindling cut from a log of the species being tested. The test load consisted of a single charge of fuel (typically 2–3 logs, 2.5–6.0 kg) being added to a quantity of hot coals, comprising 23–27% of the mass of the test load. A short period of "precombustion" was allowed before setting the test-airflow conditions followed by initiation of sampling, in a manner similar to that of Gras et al. (*20*). The precombustion ensured sustainable combustion throughout the sampling period; typically, 10–15% of the test load was pre-burnt for mid- and low- airflow conditions, with 1–5% pre-burnt for high-airflow conditions. The mass of the test load was monitored at short intervals, and sampling was terminated when the mass of the test load had been consumed or when little mass was consumed over a 10–15-min period.

Emissions were withdrawn from the center of the flue through a $^1/_8$-in. i.d. stainless steel probe using a small personal sampling pump (Q-Max, Supelco) operating at 2.50–2.60 L/min. The sampling train consisted of one or two glass-fiber filters (EPM 2000, Gelman) housed in separate 37-mm plastic cassettes, followed by a glass tube containing 150 mg of XAD-2 resin (ORBO-43, Supelco) in selected tests. Prior to sampling, the filters were dried to constant weight in a desiccator. The dilution tunnel airflow was measured using an s-type pitot tube connected to a magnehelic gauge, and monitored at short intervals (2–10 min) to ensure samples were collected isokinetically. The total tunnel volumetric flow was maintained between 5.5 and 6.0 m³/min, and corrected for the diluted flue-gas temperature. Although the gas velocity in the woodheater flue was below the measurable range of the pitot tube, the dilution factors were estimated to be of the order of 10–50. Overall tunnel-to-sample volume ratios were of the order of 2100–2300.

Background samples were collected to assess any contamination arising from the dilution air, with no target compounds detected. Build-up of creosote in the tunnel resulted in negligible amounts (<5% w/w) of some of the more volatile compounds being detected in gas-phase blanks, and were not subtracted from the test concentrations.

The potential for positive artifacts caused by gaseous adsorption onto the filters was assessed by analyzing the backup filters used in selected tests. The total mass collected on the backup filter was typically less than 4% of that on the front filter. Only a small number of compounds were detected on the backup filters, generally at levels less than 1% of those on the front filter. A small number of tests had levels of syringol, 4-methylsyringol, 4-ethylsyringol, and 4-allylsyringol up to 6% of the front filter concentrations. As the levels were all very low, no corrections were made for gaseous adsorption onto the filters.

Sample Extraction and Analysis. After sampling, the filters were again placed in a desiccator until constant weight was achieved on two consecutive readings; usually 2–3 days. They were then stored in a freezer at −18 °C until extraction, where they were cut into 2 or 3 portions; typically, $^1/_2$–$^3/_4$ of the filter was used for GC-MS analysis, with the remainder kept for future analysis. The portions were extracted in an ultrasonic bath using a series of solvents: twice with acetone, followed by one portion each of hexane, dichloromethane (DCM), and a 1:1 DCM/acetone mixture, using 15 mL of solvent for 5 min each. The extracts were combined, reduced in volume using a rotary evaporator, and filtered into autosampler vials through glass wool in a pipet.

The XAD-2 resin was extracted ultrasonically with 10 mL of a 1:1 DCM/acetone mixture followed by 10 mL of DCM. The extracts were combined and reduced in volume.

Analyses were conducted on a Varian 3800 gas chromatograph coupled to a Varian 1200 triple quadrupole mass spectrometer, scanning m/z 35–350 every 0.3 s. Analytes were separated on a Varian VF-5ms column (25 m length, 0.25 mm diameter, 0.25 μm film), using helium as carrier gas. The oven temperature was programmed from 60 to 270 °C at 6 °C/min with a final 6-min hold. Identification and quantification of peaks was based on authentic standards where possible, and on mass-spectral libraries and interpretation of mass-spectra when standards were not available. Each authentic standard was calibrated against an internal standard (nonane) for both the total-ion and quantification-ion response, and compounds lacking standards were quantified using the total-ion response of an authentic standard with a similar structure and retention time. Decane was used as a recovery standard, and averaged $64 \pm 22\%$ (mean $\pm 1\sigma$, $n = 40$) and is considered a worst case recovery as it is more volatile than the majority of target compounds, and thus no correction was made for recovery.

Results and Discussion

A total of 30 emission tests were conducted with two woodheater models, both of which were removed from use in Launceston as part of the "buyback" scheme. Although

TABLE 1. Overall Burn-Rates, Particle Emission Factors, Percentage of Particle Mass Accounted for by the Identified Particle-Phase Compounds (Mean ± 1σ), and Approximate Dilution Tunnel Temperature Range Encountered with Each Airflow Setting

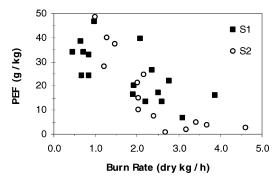|	no. tests	burn-rate (kg/h)	PEF (g/kg)	% mass accounted	dilution tunnel temp (°C)
		Heater S1			
open	7	2.70 ± 0.64	13.5 ± 4.1	18 ± 5	35−45
1/2-closed	5	1.58 ± 0.76	30.6 ± 7.6	26 ± 7	25−45
closed	5	0.72 ± 0.20	33.6 ± 9.6	30 ± 8	20−30
		Heater S2			
open	5	3.52 ± 0.71	2.86 ± 1.60	19 ± 7	45−60
1/2-closed	3	2.15 ± 0.22	12.9 ± 7.3	28 ± 9	35−50
closed	5	1.42 ± 0.44	35.7 ± 9.6	54 ± 25	30−40

FIGURE 2. Variation in particle emission factor from woodheaters operated at different burn rates.

they comprise only a small sample of the range of models available, they are representative of actual models currently used in Launceston. To assess the differences in emissions from each heater under varying airflow conditions, it was important to limit other sources of variability such as wood species and wood loading practices. It would, however, be impossible to conduct tests encompassing all operating conditions encountered across the entire city.

Particle Emissions. The overall burn rates and particle emission factors (PEF) from the two woodheaters are shown in Table 1. Heater S2 consistently had higher burn rates then S1. In fact, heater S2 operated with a closed airflow had a similar burn rate to S1 operated with a 1/2-closed airflow, indicative of the different airflow properties of the two models.

As expected, an inverse correlation between PEF and burn rate is observed for both heaters tested (Figure 2). The medium burn-rates (1/2-closed) using S2 produced PEFs intermediate between the two extremes, but for S1 they were not significantly different from the closed conditions, indicating that oxygen-starved conditions are induced much more easily with this heater. It appears that the PEF reaches a maximum at around 35−40 g/kg for most tests where the burn rate was less than 1.5 kg/h, irrespective of the heater model. A third heater model tested (results not shown because of the small number of tests) also had a PEF around 35 g/kg for a closed test (burn rate = 1.0 kg/h). The relative variability was fairly constant across all airflow settings (∼30%), and there is little differences in the PEFs between the heaters for a given burn-rate. The main difference between the heater models seems to be the variation in the burn-rate for a given airflow setting, where the secondary air inlet of heater S2 obviously allows a greater amount of oxygen into the heater.

These PEF results are slightly higher than those reported by Gras and others (20, 24), and although it appears that neither of these heaters would pass the current 4 g/kg emission limit (average of high, medium, and low burns),

these tests were not carried out in strict accordance with AS/NZS 4012 and 4013 (22, 23). Rather, the standards were used as a guide, with operating conditions altered to reflect more realistic operating conditions.

Chemical Composition of Woodsmoke. The emission factors for the organic compounds identified in this study are shown in Tables 2 and 3. Values are given as the mass of compound emitted per mass of dry wood burned, presented as means with one standard deviation. Although emissions from woodheaters have been assumed to not be normally distributed (25), standard deviations are reported here to at least give some measure of the variances encountered.

***n*-Alkanes.** The n-C_{20}−C_{26} alkane concentrations were found to be very low and highly variable, and collectively made up less than 0.5% of the total particle mass. They were also detected at inconsistent levels in blanks. As these compounds are found in emissions from other sources such as automobiles (26) and natural gas appliances (27), they are not specific tracers for woodsmoke and should be used cautiously in sourcing studies.

Furans. Substituted furan- and furaldehyde- compounds were found predominantly in the vapor-phase, although large amounts of hydroxymethylfurfural were also found in the particle-phase, comprising up to 5% of the total particle mass for the closed airflow tests.

Methoxyphenols. Substituted guaiacol- and syringol-compounds make up a large number of identified species. The most abundant compounds in this class were syringol, 4-methylsyringol, 4-ethylsyringol, syringaldehyde, and syringyl acetone. Vanillin, acetovanillone, guaiacyl acetone, and propionyl guaiacol dominated the particle-phase guaiacols, and there were large amounts of vapor-phase guaiacol, 4-methylguaiacol, and 4-ethylguaiacol. The guaiacols were generally found in smaller amounts in the particle-phase relative to their corresponding substituted syringol due to their higher volatilities.

These compounds, produced from the pyrolysis of lignin, have also been suggested as specific tracers for woodsmoke, though there is evidence to suggest that their long-term atmospheric stability may be limited (12, 28). It is therefore important that the stability of these compounds is investigated thoroughly if they are to be used as tracers in source apportionment studies.

Other Substituted Aromatic and Phenolic Compounds. Like the methoxyphenols, these compounds are also derived from the decomposition of lignin. Phenol made up 3−10% of the total mass of identified vapor-phase compounds, and other compounds with high emission rates were catechol, methoxycatechol, trihydroxybenzene, and the cresols. Significantly greater amounts of the benzaldehydes were emitted from heater S2.

Polycyclic Aromatic Hydrocarbons. This important class of compounds has been studied extensively from a multitude of combustion sources, including wood burning (25, 29). PAH emission rates determined in this study are slightly higher, but still in a range similar to those found in previous studies burning Australian woods (20, 21, 30). Levels of the particle-phase PAHs (BaA, chrysene, BaP) were relatively consistent across airflow settings and heater models, and generally below 1.0 mg/kg wood burned. Higher amounts were observed for the more volatile compounds. In particular, the high emissions of biphenyl, naphthalene, the methylnaphthalenes, and phenanthrene are noted from heater S2. This is consistent with reports that woodburning produces large amounts of the vapor-phase 2−3 ring PAHs (naphthalene−anthracene) (31). An increase in volatile PAH emissions is also observed with increasing airflow, and can be explained by the temperature dependence of their rate of formation, which increases with temperature up to 900 °C for the combustion

TABLE 2. Organic Emission Factors from Heater S1 Operated with Various Airflows (mg per kg Dry Wood Burned, Mean ± 1σ)[a]

	open		$^1/_2$-closed		closed	
	particle	vapor	particle	vapor	particle	vapor
n-Alkanes						
n-C20	0.17		0.57 ± 0.61		9.42 ± 11.9	
n-C21	0.14 ± 0.02		0.31 ± 0.14		6.41 ± 7.77	
n-C22	0.34 ± 0.09		1.73 ± 1.81		16.3 ± 2.0	
n-C23	0.40 ± 0.13		1.05 ± 0.95		20.2 ± 24.2	
n-C24	0.77 ± 0.50		1.19 ± 0.80		41.2 ± 45.9	
n-C25	1.09 ± 0.71		1.86 ± 1.30		45.9 ± 43.3	
n-C26	1.28 ± 0.99		1.11 ± 0.91		39.5 ± 33.4	
Furans						
2-methylfurfural	1.19 ± 1.97	35.4	0.56 ± 0.64	109 ± 43.4	0.51 ± 0.04	254 ± 168
hydroxymethylfurfural	343 ± 212		911 ± 750		1014 ± 453	
5-acetoxymethyl-2-furfural	6.44 ± 4.34	1.38	18.2 ± 15.8	2.07 ± 2.11	22.5 ± 8.23	4.49 ± 3.55
acetylmethylfuran	0.61	2.00		7.21 ± 3.86		16.9 ± 9.0
benzofuran		0.98		3.14 ± 1.17		3.39 ± 1.11
dimethylbenzofuran(s)		0.62		3.41 ± 1.70		5.53 ± 0.56
dibenzofuran	1.11	2.30	0.80	7.73 ± 0.52		5.05 ± 0.20
Benzaldehydes						
benzaldehyde	0.17	3.84		9.75 ± 3.54		4.91 ± 1.48
salicylaldehyde		18.7		35.9 ± 3.0		28.2 ± 11.5
p-hydroxybenzaldehyde	6.89 ± 2.73		12.5 ± 11.6		7.57 ± 5.81	
o- or m-methoxybenzaldehyde		0.37		3.50 ± 3.41		4.37 ± 1.34
cinnamaldehyde	0.29 ± 0.07	0.25	0.29	1.27 ± 0.41	0.56	1.23 ± 0.27
Guaiacols						
guaiacol	2.23 ± 4.35	24.5	2.19 ± 3.02	109 ± 74	2.02	205 ± 94
4-methylguaiacol	2.23 ± 3.87	7.39	1.90 ± 0.01	50.0 ± 39.3	7.66	80.0 ± 20.9
methylguaiacol B	0.56	1.24		7.82 ± 5.65		14.9 ± 3.6
4-ethylguaiacol	2.19 ± 2.60	5.55	7.56 ± 7.22	45.5 ± 35.2	8.38 ± 5.17	70.1 ± 1.5
4-propylguaiacol	1.66 ± 1.68	1.52	6.67 ± 6.21	11.5 ± 9.2	8.59 ± 3.85	21.2 ± 6.2
eugenol	0.81 ± 0.76		3.13 ± 2.14	3.19	2.33 ± 2.03	3.55 ± 0.19
cis-isoeugenol	0.72 ± 0.59		3.32 ± 2.71	1.08	3.41 ± 2.87	2.01
trans-isoeugenol	5.44 ± 4.00		22.6 ± 16.0		24.3 ± 17.7	1.98
vanillin	21.1 ± 10.3	0.63	49.6 ± 29.3		46.8 ± 11.4	2.09
acetovanillone	12.9 ± 6.4		37.9 ± 21.7		42.2 ± 6.5	0.53
guaiacyl acetone	32.1 ± 14.7		96.0 ± 48.1		115 ± 22	2.62
propionyl guaiacol	15.6 ± 11.3		41.1 ± 15.4		61.2 ± 50.2	
coniferyl aldehyde	10.7 ± 4.6		22.9 ± 11.4		25.2 ± 13.3	
Syringols						
syringol	183 ± 94	14.6	615 ± 305	72.5 ± 45.3	826 ± 159	128 ± 84
syringol B	2.85 ± 2.22		18.8 ± 15.3		23.3 ± 3.1	
syringol C	22.8 ± 14.1		94.9 ± 63.3		104 ± 21	
4-methylsyringol	151 ± 75	2.12	583 ± 301	20.9 ± 10.8	802 ± 155	48.8 ± 45.9
4-ethylsyringol	116 ± 54	0.98	398 ± 255	7.52 ± 3.53	696	19.4 ± 23.6
ethylsyringol B	1.19 ± 0.53		4.70 ± 3.12	0.46	7.44	0.67 ± 0.56
4-propylsyringol	16.3 ± 7.3	0.06	57.2 ± 33.1	0.28 ± 0.07	90.7 ± 23.4	2.63
4-allyl syringol	13.8 ± 6.9		40.1 ± 23.4		51.7 ± 26.2	0.77
allylsyringol B	8.40 ± 6.10		25.0 ± 10.3		36.1 ± 33.0	
allylsyringol C	26.3 ± 17.6		69.6 ± 34.4		113 ± 131	
syringaldehyde	91.0 ± 36.0		209 ± 112	0.21	225 ± 50	0.86
acetosyringone	47.0 ± 17.0		132 ± 65		165 ± 39	0.54
syringyl acetone	90.5 ± 35.9		244 ± 108		374 ± 56	1.25
propionylsyringol	5.23 ± 3.20		11.6 ± 3.1		22.8 ± 15.2	
sinapyl aldehyde	35.4 ± 13.6		78.3 ± 34.5		113 ± 66	
Other Benzenes & Phenols						
phenol	3.43 ± 6.08	27.5	4.00 ± 6.57	78.0 ± 9.69	1.04	65.2 ± 29.3
o-cresol	3.56 ± 4.17	10.8	7.03	49.7 ± 13.4		50.7 ± 26.2
m- and p-cresol	2.96 ± 4.83	10.1	7.50 ± 10.7	49.2 ± 16.3	3.74 ± 1.67	45.3 ± 18.5
4-methoxyphenol	0.54		3.04	0.38		
3-methoxyphenol	10.7 ± 0.6		21.7 ± 17.8		21.4	
2,4-dimethylphenol	1.31 ± 1.46	2.30	3.22 ± 4.39	17.5 ± 8.2	1.23 ± 0.09	21.6 ± 7.6
2,6-dimethylphenol	0.28	0.60		3.38 ± 0.70		4.48 ± 1.42
3,5-dimethoxyphenol	0.80 ± 0.47	0.17	2.03 ± 1.11	0.53	2.29 ± 0.72	
catechol	142 ± 105		467 ± 364		384 ± 30	
4-methylcatechol	34.2 ± 33.6		156 ± 132		135 ± 10	
resorcinol	11.6 ± 3.9		21.4 ± 21.8		17.4	
hydroquinone	36.9 ± 22.6		84.2 ± 75.3		55.3 ± 32.8	
5-methylresorcinol	1.22		15.2		4.81 ± 3.18	
methoxycatechol	147 ± 86		576 ± 389		636 ± 101	
ethylbenzenediol	14.3 ± 17.5		65.0 ± 67.4		56.3 ± 4.3	
o-dimethoxybenzene	0.40 ± 0.19	0.37	1.72	1.47 ± 0.75		2.77 ± 1.01

TABLE 2 (Continued)

	open		¹/₂-closed		closed	
	particle	vapor	particle	vapor	particle	vapor
Other Benzenes & Phenols, Continued						
p-dimethoxybenzene						
trihydroxybenzene	111 ± 83		300 ± 237		197 ± 76	
dimethoxytoluene		2.30		12.0 ± 6.8	21.0	19.1 ± 2.5
propiophenone	0.27				0.17	
2′-hydroxyacetophenone	0.27 ± 0.13	1.16	1.31	4.17 ± 0.97		4.80 ± 1.12
4′-hydroxyacetophenone	2.42 ± 1.48		13.7		5.29 ± 0.99	
flopropione	1.57 ± 0.96		6.20 ± 4.24		8.12 ± 1.35	
3-phenoxyphenol	4.77 ± 1.87		11.3 ± 5.3		13.2 ± 3.6	
methylcyclopentadione	13.3 ± 20.8	8.18	39.1 ± 48.1	70.6 ± 43.6	38.3 ± 27.1	110 ± 26
PAHs						
naphthalene		4.91		23.4 ± 2.8		12.7 ± 3.4
acenaphthylene		0.81		8.41 ± 0.25		4.49 ± 1.92
acenaphthene		0.13		1.71 ± 0.01		0.87 ± 0.27
fluorene	0.34 ± 0.28	0.30	0.47 ± 0.01	2.08 ± 0.10	0.36	1.33 ± 0.11
phenanthrene	4.62 ± 3.31	1.21	9.05 ± 4.53	2.61 ± 1.83	4.78 ± 1.55	1.50 ± 0.09
anthracene	0.72 ± 0.34	0.11	1.30 ± 0.55	0.28 ± 0.13	0.97	0.20 ± 0.03
fluoranthene	1.66 ± 0.91		2.62 ± 1.17	0.09	1.65 ± 0.71	
pyrene	2.49 ± 1.47		3.93 ± 1.60		2.36 ± 1.41	
benzo[a]anthracene	0.58 ± 0.31		0.84 ± 0.31		0.66	
chrysene	0.74 ± 0.38		1.09 ± 0.47		0.77	
benzo[a]pyrene	0.50	nd	nd	nd	0.14	nd
methylnaphthalene A		0.90		6.98 ± 0.57		4.27 ± 0.38
methylnaphthalene B		0.60		4.71 ± 0.55		2.79 ± 0.41
dimethylnaphthalene(s)		0.30		2.31 ± 0.62		1.84 ± 0.18
trimethylnaphthalene(s)		0.14		1.77 ± 0.83		1.87 ± 0.62
1-naphthol			29.8		4.73	
2-naphthol	5.77 ± 4.32		18.0 ± 8.1		9.58	
biphenyl						
Sugars						
levoglucosan	738±209		2026±1017		3424±1310	
1,4:3,6-dianhydro-β-D-glucose	76.5±25.4		246±150		272±63	
Maltols						
maltol	20.8 ± 17.9	3.03	68.7 ± 55.4	12.7 ± 9.7	69.2 ± 33.2	18.8 ± 1.1
5-hydroxymaltol	69.1 ± 33.4		231 ± 154		218 ± 75	0.90
hydroxymaltol B	1.40 ± 1.21		6.22 ± 4.80		7.45 ± 4.47	0.77
hydroxymaltol C	2.39 ± 1.69		7.07 ± 3.23		11.5 ± 7.3	

[a] nd, not determined.

of phenols and lignin (*32*). The higher temperatures encountered when using S2 compared to S1 (especially with an open airflow setting, discussed later) also explains the higher PAH emissions from this heater. The results from this study are in contrast to those from a previous study undertaken in Australia (*30*), in which PAH emissions were higher for slower burning conditions. Morawska and Zhang (*33*), however, note that while the total organic emissions decrease, the proportion of PAHs increases with increasing burn rate.

PAHs have been used in CMB models in the past (*34*), but because they are produced by many different sources and degrade during atmospheric transport, they cannot be reliably used as tracer compounds. Their use for tracing woodsmoke in particular may be very limited, as photolytic degradation of PAHs is enhanced in the presence of methoxyphenols (*35*).

Levoglucosan. The single most abundant compound associated with woodsmoke was levoglucosan (1,6-anhydro-β-D-glucopyranose), comprising 5−16% of the total particulate mass (Table 4). Previous studies have found it to comprise a similar proportion (*17, 18*). As woodburning is the only known source of levoglucosan, its abundance and high environmental stability (*36*) make it an excellent general tracer for biomass combustion. Its resistance to degradation is so great it has even been analyzed in sediment cores to trace historical forest fires over the past 7000 years (*37*).

Silylation of levoglucosan has been required in a number of previous studies to make it more amenable to GC−MS analysis. It was successfully quantified in this study, without derivitisation, by selecting the base peak m/z 60. Reducing sample handling and pretreatment in this way minimizes the potential for losses or contamination, while at the same time providing considerable time and cost savings. Silylation is still required when targeting some of the more-highly polar compounds found in woodsmoke such as resin acids, sterols, and the higher alcohols (*12*). Another sugar tentatively identified was 1,4:3,6-dianhydro-β-D-glucose.

Maltols. Compounds based on maltol (3-hydroxy-2-methyl-4-pyrone) were found partitioned between the particle- and vapor-phases, depending on the airflow setting. These compounds have not been reported in previous woodsmoke characterization studies, however maltol itself has been described in smoke flavorings for food (*38*). They are probably produced from the breakdown of cellulose, and may also be specific tracers for wood burning, although their presence in emissions from other sources and atmospheric stability should be investigated.

Individual Organic Compound Emission Factors. The proportion of the particulate matter (PM) mass accounted for by the identified particle-phase compounds increased as the airflow setting was progressively closed (Table 1). While many of the differences are not significant at one standard deviation, the general trend holds for both heater models. The higher temperatures and greater oxygen availability encountered with the open tests presumably lead to a larger proportion of the organic compounds being burned, which

TABLE 3. Organic Emission Factors from Heater S2 Operated with Various Airflows (mg per kg Dry Wood Burned, Mean $\pm$ 1σ)[a]

	open		½-closed		closed	
	particle	vapor	particle	vapor	particle	vapor
_n_-Alkanes						
_n_-C20					6.51 ± 8.94	
_n_-C21					0.37	
_n_-C22			1.25		3.64 ± 3.02	
_n_-C23	0.05		1.23		1.84 ± 1.17	
_n_-C24			0.07		0.53	
_n_-C25					0.76	
_n_-C26						
Furans						
2-methylfurfural		149	0.51	545 ± 750	2.12 ± 2.28	150 ± 76
hydroxymethylfurfural	9.3 ± 12.0	358	392 ± 412	157 ± 189	1809 ± 1040	40.5 ± 38.7
5-acetoxymethyl-2-furfural	0.40	25.5	5.45 ± 7.86	70.1 ± 93.1	42.4 ± 34.1	10.2 ± 1.1
acetylmethylfuran		15.0		60.4 ± 83.3	1.29	16.2 ± 8.6
benzofuran		7.58		10.4 ± 13.6		1.91 ± 0.32
dimethylbenzofuran(s)		4.23		25.7 ± 35.5		6.66 ± 3.51
dibenzofuran		44.0		51.4 ± 68.1		5.11 ± 1.81
Benzaldehydes						
benzaldehyde		41.8		29.2 ± 37.0		4.42 ± 1.93
salicylaldehyde		122		161 ± 211		14.4 ± 16.4
_p_-hydroxybenzaldehyde	2.80 ± 3.27	3.69	7.00 ± 5.60		18.8 ± 13.3	
_o_- or _m_-methoxy benzaldehyde		12.0		29.6 ± 41.4		37.8 ± 44.3
cinnamaldehyde		6.84		14.4 ± 19.8	0.97 ± 0.90	1.76 ± 0.01
Guaiacols						
guaiacol	0.06	118	0.81 ± 1.07	730 ± 1015	19.5 ± 23.5	179 ± 90
4-methylguaiacol	0.07	45.7	0.21	406 ± 566	5.48	110 ± 48
methylguaiacol B		5.21		64.2 ± 89.3		18.9 ± 8.5
4-ethylguaiacol	0.11	42.9	1.68 ± 1.81	394 ± 549	21.1 ± 25.0	107 ± 46
4-propylguaiacol		11.8	2.52	150 ± 209	20.8 ± 24.9	39.9 ± 10.9
eugenol		4.59		30.6 ± 42.4	9.41	7.34 ± 0.01
cis-isoeugenol			0.92		6.33 ± 5.54	2.87
trans-isoeugenol	0.17		4.03 ± 4.12		41.8 ± 31.2	0.62
vanillin	3.65 ± 2.60	33.4	22.4 ± 18.0	45.8 ± 59.0	96.4 ± 55.0	8.75 ± 2.76
acetovanillone	2.79 ± 2.06	8.41	15.3 ± 13.8	5.22 ± 6.14	75.1 ± 40.4	1.35 ± 1.18
guaiacyl acetone	8.01 ± 5.90	20.9	47.0 ± 47.9	26.3 ± 33.5	199 ± 87	8.08 ± 2.47
propionyl guaiacol	0.71 ± 0.27	2.12	5.53 ± 4.97	0.43	60.4 ± 32.9	
coniferyl aldehyde	2.99 ± 0.28		10.3 ± 6.4		44.2 ± 30.5	0.86
Syringols						
syringol	6.47 ± 6.03	327	211 ± 266	1285 ± 1733	1257 ± 482	208 ± 56.6
syringol B	0.15		5.56 ± 7.95	4.10	50.9 ± 29.0	1.57
syringol C	2.11 ± 0.59	6.41	29.2 ± 35.1		203 ± 105	2.35
4-methyl syringol	6.98 ± 4.36	89.1	190 ± 216	430 ± 568	1194 ± 477	91.6 ± 43.9
4-ethyl syringol	5.83 ± 3.63	55.6	125 ± 137	198 ± 257	878 ± 510	42.4 ± 21.9
ethyl syringol B			0.58	7.62 ± 10.5	10.8 ± 5.5	1.41 ± 0.62
4-propylsyringol	1.04 ± 0.48	5.49	16.1 ± 16.2	12.4 ± 15.7	138 ± 79	3.19 ± 2.43
4-allylsyringol	1.41 ± 0.25		10.6 ± 8.7	0.86	73.1 ± 37.9	1.63 ± 1.56
allylsyringol B			4.48 ± 4.44		38.4 ± 16.3	
allylsyringol C	0.97 ± 0.49		3.40 ± 2.56		42.4 ± 32.2	
syringaldehyde	25.8 ± 2.7		97.4 ± 54.4	1.66 ± 1.74	400 ± 215	4.35 ± 5.12
acetosyringone	12.4 ± 2.9		53.2 ± 38.8		265 ± 133	2.36 ± 3.06
syringyl acetone	22.8 ± 5.7	1.35	113 ± 99		479 ± 177	5.68 ± 6.90
propionylsyringol	1.74 ± 0.54		4.24 ± 3.49		18.1 ± 6.8	0.90
sinapyl aldehyde	13.0 ± 1.9		36.5 ± 21.9		131 ± 89	3.54
Other Benzenes & Phenols						
phenol	0.26	317	0.86 ± 1.14	415 ± 556	10.2 ± 14.0	65.5 ± 10.0
_o_-cresol		121		248 ± 340	17.1	44.8 ± 7.6
_m_- and _p_-cresol	0.21	144	0.83 ± 1.26	297 ± 406	17.8 ± 21.6	52.8 ± 4.34
4-methoxyphenol			0.87		5.55	1.36
3-methoxyphenol				42.8 ± 55.2	34.9 ± 27.4	4.32
2,4-dimethylphenol		45.1	0.45 ± 0.55	162 ± 224	8.07 ± 11.0	31.6 ± 8.5
2,6-dimethylphenol		6.37		24.7 ± 34.9		5.77 ± 2.24
3,5-dimethoxyphenol			0.86 ± 0.87	3.46 ± 4.54	7.25	0.67 ± 0.15
catechol	27.0 ± 33.7	136	193 ± 223	60.6 ± 73.9	814 ± 414	12.5 ± 14.5
4-methylcatechol	8.20 ± 10.2	4.64	57.9 ± 68.7	0.34	248 ± 132	3.62
resorcinol	5.11		16.5 ± 7.7		28.1 ± 19.8	
hydroquinone	12.8		41.7 ± 45.9		150 ± 100	
5-methylresorcinol	0.41		2.75 ± 2.95		7.21 ± 7.18	
methoxycatechol	9.15 ± 6.58	15.0	194 ± 235	75.5 ± 101	1255 ± 606	27.8 ± 28.8
ethylbenzenediol	7.22		23.9 ± 32.1		106 ± 60	
_o_-dimethoxybenzene		3.33		6.75 ± 9.26		3.28 ± 1.23

TABLE 3 (Continued)

	open		¹/₂-closed		closed	
	particle	vapor	particle	vapor	particle	vapor
Other Benzenes & Phenols, Continued						
p-dimethoxybenzene						
trihydroxybenzene	5.66		134 ± 200		531 ± 374	
dimethoxytoluene		11.2		93.0 ± 128		26.5 ± 10.7
propiophenone						
2′-hydroxyacetophenone		18.5		51.4 ± 70.2		10.2 ± 0.8
4′-hydroxyacetophenone	1.73		3.25 ± 2.24		9.69 ± 0.93	
flopropione	0.25 ± 0.08		1.89 ± 2.18		14.9 ± 7.7	
3-phenoxyphenol	1.28 ± 0.28		4.93 ± 2.89	0.61	23.4 ± 10.0	
methylcyclopentadione	0.52 ± 0.28	83.7	4.13 ± 6.05	514 ± 717	100 ± 141	126 ± 31
PAHs						
naphthalene		118		77.7 ± 101		7.05 ± 3.53
acenaphthylene		61.9		37.8 ± 50.3		2.31 ± 2.71
acenaphthene		6.88		7.91 ± 10.8		0.85
fluorene		16.1		12.3 ± 16.3		1.32 ± 0.82
phenanthrene	0.34 ± 0.40	97.3	1.82 ± 1.95	21.6 ± 24.5	5.54 ± 3.04	1.35 ± 1.50
anthracene		10.8	0.29 ± 0.21	2.22 ± 2.56	0.67	0.27
fluoranthene	1.59 ± 1.08	5.83	1.10 ± 0.28	0.32	1.36 ± 1.01	0.09
pyrene	2.91 ± 2.02	7.14	1.64 ± 0.24	0.30	2.27 ± 1.90	0.13
benzo[a]anthracene	0.67 ± 0.41		0.36 ± 0.06		0.34	
chrysene	0.83 ± 0.59		0.47 ± 0.07		0.67	
benzo[a]pyrene	0.55 ± 0.42	nd	0.39 ± 0.11	nd	0.22 ± 0.10	nd
methylnaphthalene A		22.5		29.4 ± 39.3		3.68 ± 0.32
methylnaphthalene B		15.7		19.8 ± 26.4		2.28 ± 0.32
dimethylnaphthalene(s)		4.42		12.5 ± 17.0		2.08 ± 0.30
trimethylnaphthalene(s)	0.12	2.48		11.8 ± 16.5		2.03 ± 0.46
1-naphthol	1.50	3.91	4.38 ± 2.99	1.64 ± 1.78		0.37
2-naphthol	2.51 ± 2.32	13.0	5.68 ± 3.75	0.75	10.7 ± 5.9	
biphenyl		75.3		86 ± 116		9.22 ± 0.76
Sugars						
levoglucosan	620 ± 320	26.7	1533 ± 872	5.76 ± 6.73	5216 ± 2843	86.5 ± 112.4
1,4:3,6-dianhydro-β-D-glucose	18.0 ± 13.2	57.3	105 ± 93	58.5 ± 72.6	456 ± 247	11.7 ± 8.9
Maltols						
maltol	1.01	75.1	12.1 ± 19.0	180 ± 247	148 ± 128	39.2 ± 3.5
5-hydroxymaltol	1.05 ± 0.64	42.9	81 ± 105	22.8 ± 28.6	415 ± 313	7.85 ± 8.96
hydroxymaltol B			1.55 ± 1.64		14.8 ± 13.9	
hydroxymaltol C		59.2	1.91 ± 2.13	28.2 ± 34.5	17.5 ± 10.5	11.2 ± 12.6

[a] nd, not determined.

TABLE 4. Particle-Phase Levoglucosan Emission Factors (mg/kg Wood Burned) and Mass Fractions (mg/g PM) in Woodheater Emissions (Mean ± 1σ)

	emission factor (mg/kg)		mass fraction (mg/g)	
	S1	S2	S1	S2
open	738 ± 209	620 ± 320	52 ± 20	137 ± 50
¹/₂-closed	2026 ± 1017	1533 ± 872	65 ± 19	123 ± 31
closed	3424 ± 1310	5216 ± 2843	95 ± 38	160 ± 91

may be consistent with the fact that a greater proportion of elemental carbon is produced at higher burn temperatures (6).

Just as the model and airflow setting affected the particle emission factor, these factors also appear to affect the emission rates of most of the organic compounds. It can be seen from Tables 2 and 3 that there is a general trend of increasing particle-phase organic emission factors as the airflow is progressively closed. The less efficient combustion conditions and lower temperatures encountered when operating with a closed airflow leads to increased particle-phase organic emissions. There are also distinct differences between the heater models. Generally, for the open and ¹/₂-closed airflows, S1 produced about 10 and 3 times the amounts of organic compounds than S2, respectively, while S2 with a closed airflow created around 1.5 times the amount of organics than S1. These inconsistencies could be due to

the different designs of the two heaters, where the secondary combustion zone of S2 does not work effectively at the lower temperatures encountered when the airflow is fully closed. The variation in organic emission factors between the airflow conditions also appears smaller for S1 than S2, consistent with the PEF results.

In contrast to the particle-phase trends, the emission factors of some vapor-phase compounds were found to increase with the open airflow, particularly for heater S2. Much of the observed increase can be attributed to the higher firebox and emission temperatures, and thus higher dilution tunnel temperatures (Table 1), encountered during the open airflow tests leading to greater partitioning of some semi-volatile compounds to the vapor-phase. This also partially explains the reduction in the particle-phase composition for the open airflow tests. However, increased levels of many of the volatile compounds found only in the vapor-phase are observed (e.g., phenol, cresols and benzofuran, naphthalene). Similar observations have been noted previously (11). It is likely that the higher firebox temperatures would lead to greater volatilization of these compounds from the wood itself, with the higher airflow then quickly removing these vapors before they could combust. This is certainly the case early in the burn cycle, as total volatile-organic-compound emissions are greatest within the first 15−30 min (20).

Differences in Emission Behavior with Changes in Reporting Unit. Although it is general practice to report woodheater emissions in terms of the mass of wood burned,
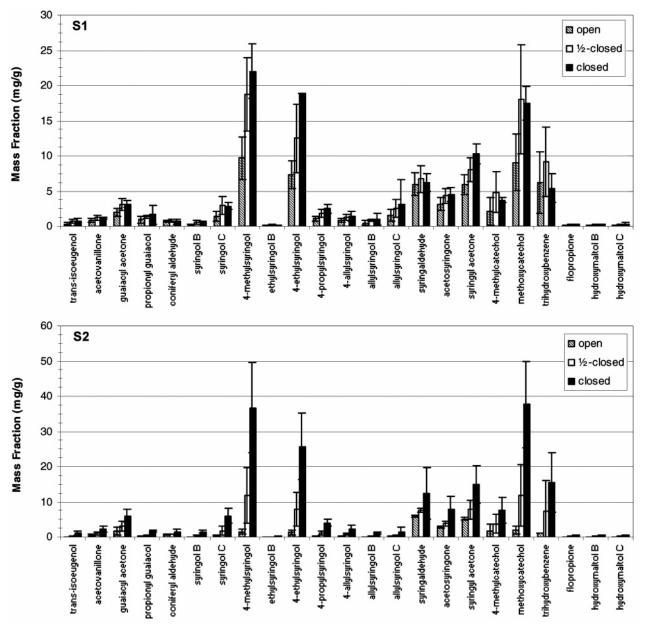
FIGURE 3. Mass fraction (mg compound per g PM) of selected particle-phase organic compounds present in emissions from woodheaters operated with different airflow conditions.

the data for each compound must be converted to the fraction of total particle mass to be used in receptor models.

A number of compounds show different trends depending on the reporting unit. For example, the emission factors for propionyl syringol and hydroquinone increase greatly with decreasing airflow settings (1.7−19.2 and 12−160 mg/kg wood burned, respectively, for heater S2) but their proportions relative to the mass of particle emitted remains fairly constant (0.41−0.63 and 2.6−5.1 mg/g PM).

Another compound for which mass fraction does not vary with burn rate is levoglucosan (Table 4). There is some difference between heater models, however, but this is only slightly greater than one standard deviation. The greater proportion produced from heater S2 may be due to the lower amount of other organic compounds produced by this heater, thus increasing the mass fraction of levoglucosan. A third model tested (results not shown because of the small number of tests) had levoglucosan emissions of around 60−80 mg/g PM, again irrespective of the airflow conditions. There is a clear need for further testing to gauge the extent of this

variation. Despite the small variations observed, levoglucosan has the potential to be used as a general tracer for woodsmoke.

Other studies have also reported that the mass fraction of levoglucosan is relatively constant irrespective of the species of wood burned (98−168 mg/g organic carbon), although softwoods tended to exhibit slightly lower values (36−95 mg/g organic carbon) (*17, 18*). This uniformity in levoglucosan emissions could simplify the determination of the biomass contribution to atmospheric pollution to a simple ratio calculation. Schauer et al. (*13*) used a similar principle to determine the woodheater contribution to ambient benzene, ethene, and acetylene.

A similar concept is employed when using carbon-14 as a tracer for determining biomass and fossil fuel contributions to air pollution, where the ^{14}C content of the particles is directly related to the proportion of biomass input (*39, 40*). This method is sometimes used to complement or confirm CMB results (*41, 42*). The high cost of analysis has prevented it from being routinely used, and it can be complicated by other noncombustion sources of ^{14}C such as cooking of food

and vegetative detritus. The relative ease of determination coupled to its tracer-like qualities may make levoglucosan a cheaper and much easier alternative to ^{14}C in determining total woodsmoke contributions to ambient aerosols.

In contrast to levoglucosan, other compounds exhibit variations in their emitted mass fractions with changes in the airflow setting (Figure 3). As source apportionment studies generally focus on particulate matter only, results have been restricted here to compounds found predominantly in the particle-phase across all heaters and airflow conditions. This was also necessary to remove the effect of the dilution-tunnel temperature on the partitioning of semi-volatile compounds. As for the emission factors, there is a trend of increasing proportions of organic compounds as the airflow is progressively decreased. The higher temperatures encountered in the open airflow tests appear to break down a larger proportion of the particle-phase organic compounds relative to the mass of particles emitted. So not only do woodheaters operating with an open airflow produce less mass of particles per kg of wood consumed, they also produce less mass of particle-phase organics per gram of emitted particulate matter.

This study has presented emission factors for nearly 100 organic compounds emitted from woodheaters under different airflow conditions. Emission factors for the majority of particle-phase compounds increased as the airflow was closed, while levoglucosan was found to vary relatively little.

Acknowledgments

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