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CHARACTERIZATION OF PM_{2.5} FROM RESIDENTIAL WOODSTOVE USE FOR SOURCE APPORTIONMENT APPLICATION

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Master of Science
in Chemistry

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Abstract

Porden, Virginia, M.S., Summer 2015

Chemistry

Chairperson: Christopher Palmer

Results are presented for the comparative analysis of the PM_{2.5} (Particulate Matter <2.5 μm) emissions from an EPA certified and a Traditional style wood stove using western larch. A total of 92 Quartz QMA 47mm filters were collected using a BGI PM_{2.5} SSC (Sharp Cut Cyclone) sampler from each stove type and analyzed on a gas chromatograph-mass spectrometer against blank and deuterated internal standards. The results were analyzed using a Welch's t-test ($\alpha > 0.05$) to statistically differentiate between stove designs for temperature, mass, levoglucosan, resin acids (abietic and dehydroabietic), and polycyclic aromatic hydrocarbons [PAH] (acenaphthene, anthracene, benz(a)anthracene, pyrene, and retene). There was no statistical difference in levoglucosan PM_{2.5} mass fraction between the stove types, yielding a mean levoglucosan fraction of 9.25% and 95% confidence interval of 8.43% to 10.25%. This suggests a uniform breakdown of cellulose to levoglucosan without considerable secondary byproducts regardless of wood stove design, and a 95% confidence interval for the conversion factor to calculate total woodstove PM_{2.5} from levoglucosan. Significant differences were observed for the resin acids, which both yielded smaller fractions in the EPA stove than the traditional, and for mean stove operating temperatures, the EPA stove was between 55.9°C and 102.3°C higher than the Traditional stove. Mass and PAH results require more data in order to be clearly interpreted with respect to this study. These results, along with previously published studies, add to the body of knowledge regarding EPA and traditional wood stove analysis and wood combustion conversion factors for use in source apportionment studies.

Introduction

The combustion of biomass as a heating fuel is a significant worldwide source of particulate matter with a diameter of 2.5 μm or less, more commonly referred to as $\text{PM}_{2.5}$ (Naeher, Brauer et al. 2007). Over 2.2 million homes in the U.S. currently use woodstoves as their primary heating source, of which the majority are old, inefficient models (Energy 2009). Wood smoke from residential wood stoves during winter months is the single largest source of air pollution annually in the Northern Rocky Mountains, where average annual usage is 2,100 hours of wood combustion per wood burning device (EPA 2005). Despite EPA guidelines initially established in 1988 that set emission rates for catalytic (4.1 grams per hour [g/h]) and non-catalytic (7.5 g/h) woodstoves, both old and new wood burning stoves continue to be significant sources of ambient $\text{PM}_{2.5}$ (Larson, Gould et al. 2004, Ward, Hamilton Jr et al. 2004, Naeher, Brauer et al. 2007, Ward and Lange 2010). Widespread use of wood stoves, especially in areas with high population density, can result in elevated and sustained $\text{PM}_{2.5}$ exposures both outdoors and *within* homes (Ward and Noonan 2008, Noonan, Ward et al. 2011, Ward, Boulafentis et al. 2011).

The associated health risks of prolonged or elevated exposure to $\text{PM}_{2.5}$ vary depending on the complexity of particulates in the fine fraction ($\text{PM}_{2.5}$). Once past the initial protective mechanisms of the airways, $\text{PM}_{2.5}$ will accumulate in membranes and have adverse health effects on the lungs, heart, and epithelium. Increased risks of asthma, cardio and respiratory mortality and morbidity, as well as complications in cardiotoxicity diagnosis are seen in areas of high $\text{PM}_{2.5}$ exposure. Chronic exposure to $\text{PM}_{2.5}$ is known to cause significant adverse health effects, including respiratory illness, multiple forms of cancer, and eventual mortality, all of which are based on the chemical makeup and concentration of the particulates (Jalava, Happonen et al. 2012). Alterations in the ion channel function of cardiomyocytes and QT prolongation have been observed in those at risk (Klaassen, Casarett et al. 2013). Resin acids are known carcinogens and PAHs, which are components of $\text{PM}_{2.5}$ from biomass combustion, can be oxidized in the liver, producing hydroxylated compounds and carcinogenesis. This has strong implications for any populated area with adverse environmental conditions with regards to air quality.

Apportionment of $\text{PM}_{2.5}$ to specific combustion sources is important to U.S. communities in nonattainment with EPA standards for ambient $\text{PM}_{2.5}$ (a three year average of $\leq 12 \mu\text{g}/\text{m}^3$ (annual standard) or $\leq 35 \mu\text{g}/\text{m}^3$ within a 24 hour period (EPA 2012)), as it provides guidance regarding the sources and composition of the particulates and the possible impact of high exposure rates or prolonged exposure times. Apportionment also provides guidance for mitigation efforts, allowing communities to focus on reduction in emissions from the most significant sources. Source apportionment is typically accomplished using the chemical mass balance approach, which utilizes inorganic and organic source profiles of the ambient $\text{PM}_{2.5}$ and multiple representative sources. (Ward, Trost et al. 2012)

Household wood combustion is responsible for adverse air quality on a global scale, with levels similar to those measured in heavy traffic. The fuel being burned has a significant effect on the particulates produced as does the device in which the combustion is being completed. Therefore an important balance must be struck

between increasing the energy output and decreasing the harmful byproducts of any such device. Here it is important to note that more complete combustion does not necessarily mean a decrease in adverse health effects, merely a different subset of compounds that need to be assessed and characterized. These differences were assessed in Europe by looking at several new and old heating devices commonly found in that area and assessing the burn conditions of each device, as well as the toxicological effects of their respective emissions. The resulting inflammatory response and chemical profiles of these devices showed significant differences in their response ratios. While the inflammatory response was significantly higher with the older combustion devices, the chemical profiles showed increased metal and PAH concentrations (upwards of a 300 fold difference) with the new wood stoves. When normalized for comparison, these results suggest that health effects are specifically related to the combustion device producing the PM_{10} . (Jalava, Happonen et al. 2012)

Previous studies suggest that significant differences in the chemical composition of $PM_{2.5}$ result from stove design, specifically differences in older traditional style wood stoves and newer EPA certified wood stoves (Bergauff, Ward et al. 2009), as well as wood fuel type (Fine, Cass et al. 2004), and stove airflow settings (Jordan and Seen 2005). However, no controlled study of the chemical composition of $PM_{2.5}$ emissions from these different stove designs has yet been conducted.

This study seeks to measure, compare, and demonstrate the utility of $PM_{2.5}$ chemical profiles of two representative wood stoves. Emissions from an EPA certified wood stove (noncatalytic) and a traditional wood stove design (Figure 1) were collected under controlled conditions to generate source profiles of $PM_{2.5}$ emissions. The results and information gained in this study will serve two purposes: a) the profiles generated will be useful to inform follow up studies of the health effects of $PM_{2.5}$ exposure in order to assess long and short term exposures to $PM_{2.5}$ emissions from different stove types and b) for apportionment of ambient $PM_{2.5}$ based on organic molecular composition. Application of these apportionment findings can be conducted on previous nonattainment

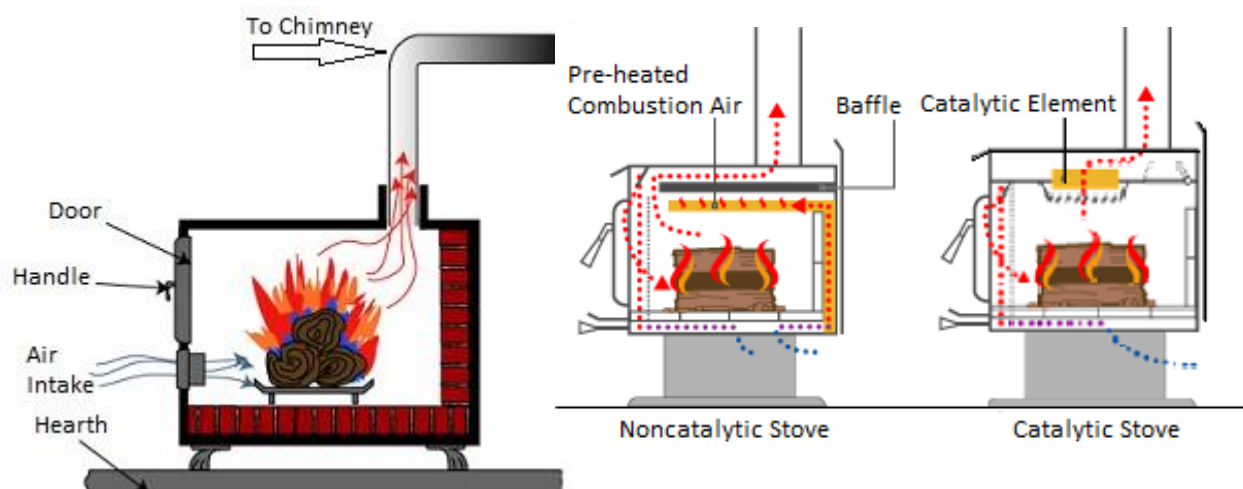


Figure 1: (From right to left) Traditional wood stove design, EPA certified noncatalytic wood stove design, EPA certified catalytic wood stove design.

study areas where PM_{2.5} data has already been collected, including Libby, MT and Fairbanks, AK. Study results can be applied to new legislation under consideration by the EPA to further restrict guidelines, requiring improved efficiency on wood burning devices (~1.4 g/hour) and stricter standards on community air pollution levels that are directly impacted by wood burning stoves.

Background Literature

The United States have become increasingly aware of the differences in wood stove types and how they contribute to air quality and health impacts (McClure 2011). This has resulted in several wood stove change out programs including Libby, MT and the Nez Perce Reservation in Idaho, each of which have yielded significant changes in air quality as assessed before and after the wood stove change outs were implemented (Ward and Noonan 2008, Bergauff, Ward et al. 2009, Ward, Boulafentis et al. 2011).

Ambient and indoor air in Libby, MT was monitored during a comprehensive wood stove replacement program. Researchers observed decreases in overall ambient PM_{2.5}, levoglucosan (-50%), and PAHs (-64%) (Ward, Palmer et al. 2009), as well as increases in the levels of resin acids (Bergauff, Ward et al. 2009). These results suggest significant differences in the composition of general emissions from the two stove types, but further investigation is needed to understand the differences in emissions.

A controlled study of emission composition was conducted using Australian devices and wood fuels, finding significant differences in the chemical composition of PM_{2.5} depending on device type, but identifying burn conditions as having a more significant impact on PM_{2.5} composition (Jordan and Seen 2005). The layout for the collection facility they used can be seen in Figure 2 and compared to Figure 3. No such study has been conducted to compare emissions from various woodstove devices in the U.S.

A series of source tests from fireplace combustion compared the fine particulate emission factors for 10 wood species to determine differences in molecular tracers between species across the United States. By assuming that people burn the wood that is available to them, Fine, et al. 2004 established an availability index associated

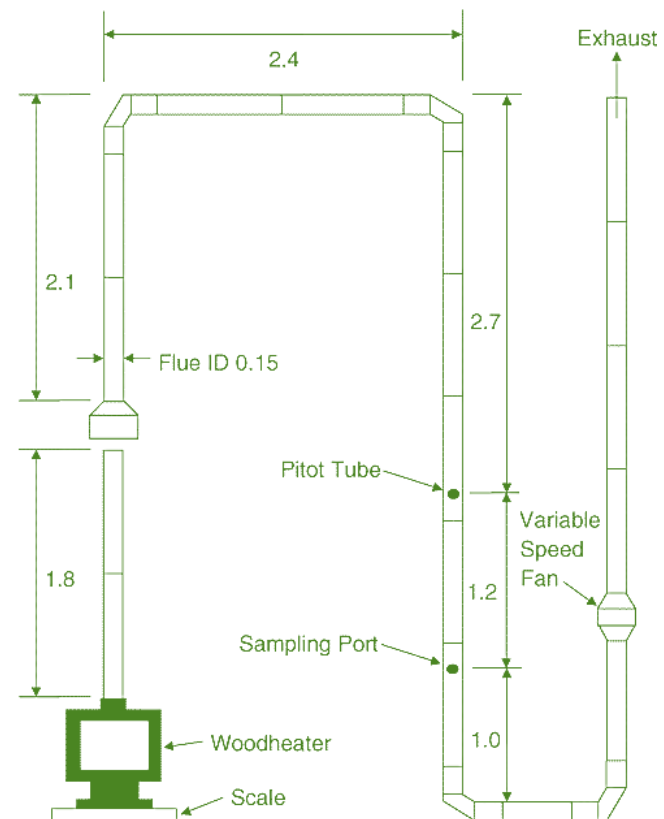


Figure 2: Woodheater dilution tunnel setup (dimensions are in meters). (Jordan and Seen 2005).

with moisture content, geographical range, and emission factors for over 300 compounds. This work reaffirmed the use of levoglucosan, lesser amounts of other sugar derivatives, and potassium as specific tracers (or chemical markers) for biomass burning, and provided the basis for distinguishing emission characteristics from burning different tree species (Fine, Cass et al. 2004).

Recent studies suggest that apportionment of ambient PM to biomass combustion sources can be accomplished at less expense than that of the full chemical mass balance approach by using the levoglucosan content of collected ambient PM (Caseiro, Bauer et al. 2009, Giannoni, Martellini et al. 2012). Levoglucosan is used as a source-specific marker for biomass combustion. In order to apportion PM to any source or sources using such an approach, one must know the source-specific emission factors for the marker of interest. Caseiro went on to define a specific relative contribution of wood smoke to the total PM_{2.5} load, as defined in the following equation:

$$\text{Wood smoke PM}_{2.5} = \text{Levoglucosan} \times 10.7 \quad (\text{Caseiro, Bauer et al. 2009})$$

Levoglucosan is considered highly appropriate for apportionment to biomass combustion due to its relatively high concentration in emissions and its high specificity. However, additional compounds such as mannosan, galactosan, resin acids, methoxyphenols, and certain polycyclic aromatic hydrocarbons (PAH) are prevalent in emissions from wood stoves and may be suitable as either primary or secondary markers for use in source apportionment development. In this study we selected levoglucosan, resin acids and PAHs for wood smoke analysis. These specific compounds were selected to be analyzed due in part to their known prevalence in wood smoke particulate (Fine, Cass et al. 2004) and, in the cases of the resin acids and PAHs, their potential impact on acute and chronic PM_{2.5} toxicity. Levoglucosan was selected over mannosan and galactosan because it is the prevalent compound compared to other sugars in most source apportionment analysis with regards to wood fuel. The methoxyphenols were omitted from analysis because of their semivolatility and in the results from Libby, MT those levels were more closely related to ambient temperatures than with emissions.

Methods

Experimental Design

The University of Montana, Center for Environmental Health Sciences (CEHS) has established a facility for the generation and collection of wood stove particulate emissions which allows for controlled burn rate, fuel type (western larch with 15% moisture), air flow, and proper device operation. A diagram of the wood smoke generation and sampling system is presented in Figure 3. Smoke is collected from the chimney of either an EPA certified (Quadra-Fire 2100 Millennium) or traditional style (England Stove Works) woodstove and is pumped into mixing chamber #1 where it is mixed with 10% filtered ambient air. Fresh air, mixed air, and temperature sensor feeds are directed to the indoor portion of the facility where the smoke is further diluted and animal exposures are conducted.

Samples of emissions were collected using 47mm quartz filters. These filters were prepared before sampling in accordance with guidelines established by Chester LabNet, in which they were pre-fired at 500°C for 2.5 hours in a muffle furnace, placed in filter cassettes, and then stored at 4°C. Filters were weighed pre- and post-sampling with three repetitions under controlled temperature (74°F/ 23.3°C) and humidity (35% Relative Humidity) conditions using a Mettler Toledo MT5 balance.

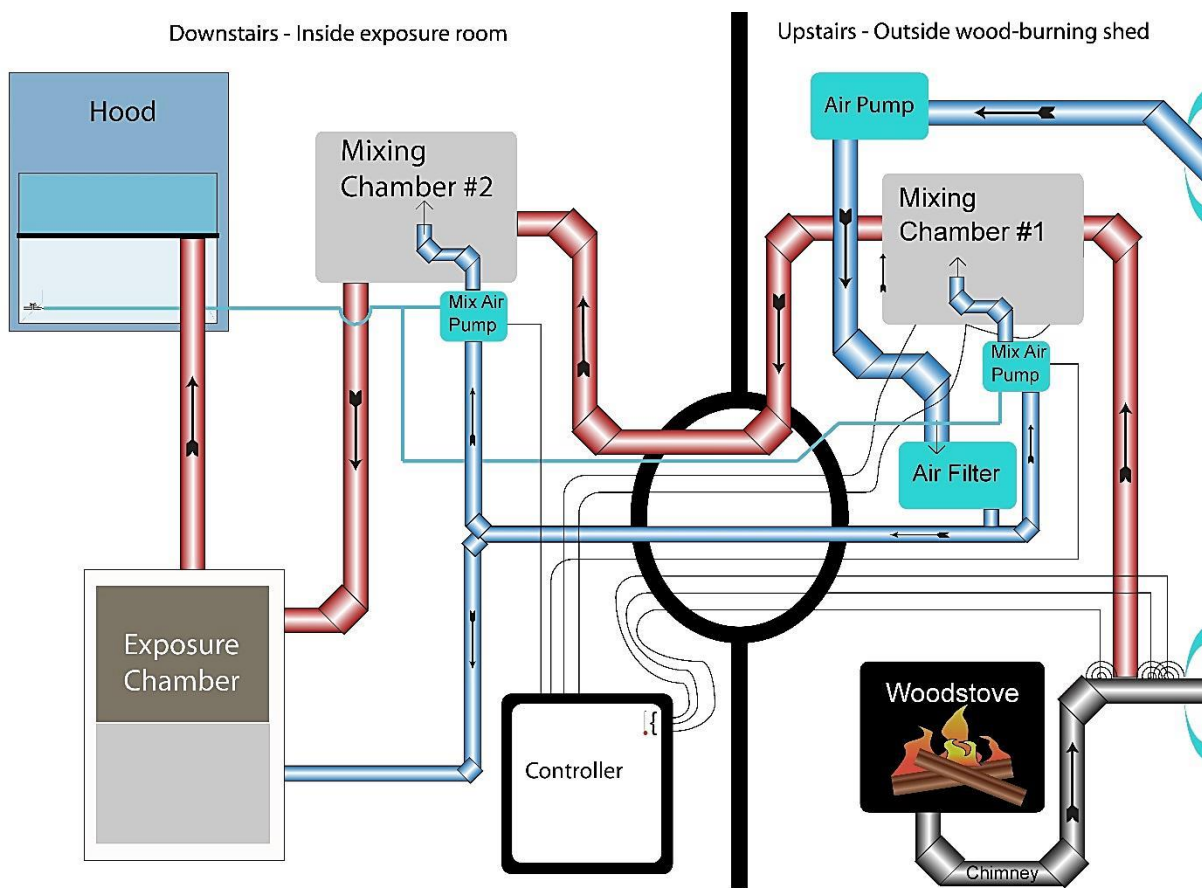


Figure 3: CEHS wood stove and inhalation study facility. Red pathways represent particulate air pathways; blue represent ambient air pathways; black lines represent monitoring and control sensors. (Matthew Ferguson, 2014)

Sampling

Quartz QMA filter samples (47mm) were collected from Mixing Chamber #1 in the CEHS facility using a BGI PM_{2.5} SSC sampler attached to a pump set at ~16.25 L/min. The pump flow rate was measured at the beginning and end of each sample collection, and did not fall below 16.09 L/min for any event. A set of 92 samples ($n_{EPA} = 47$, $n_{TRAD} = 45$) were analyzed for exactly 15 minutes each once the fire was established in each device. Stove temperature was monitored using a Raytek MiniTemp Infrared (IR) Thermometer every 15 minutes, corresponding to one reading per filter. Approximately 243.75 liters of air (average 16.25L/min) for 15 minutes per sample) were sampled per filter. Burn conditions were maintained throughout sampling by maintaining a low,

steady flame in the device to sustain combustion above 150°C. Average temperature within the burn shed was recorded as $30.6 \pm 5.6^\circ\text{C}$. Blank filters were collected for every 10 filters by following the same procedure, but without connection to mixing chamber #1. After exposure, samples were maintained at 4°C until analysis was completed for levoglucosan, resin acids, and polycyclic aromatic hydrocarbons.

Chemical Analysis

Quartz filter samples were analyzed using methods previously reported by M. Bergauff and T. Ward (Bergauff, Ward et al. 2009). Filters were removed from cold storage and allowed to come to room temperature before being cut in half using a Fiskars 1" rotary cutter and placed in a 30 mL vial. One half of each filter was spiked with deuterated internal standards (Table 1) which were allowed to absorb onto filters for 30 minutes before compounds were extracted from filters with sonication into ethyl acetate containing 3.6 mM triethylamine in a Cole-Palmer Ultrasonic Cleaner, model 08895-04. The volume of the solution was evaporated to dryness in a sand bath and then rehydrated with ethyl acetate, qualitatively transferred to a centrifuge vial, and derivatized on a sand bath for one hour with bis(trimethylsilyl)trifluoroacetamide (BSTFA), trimethylchlorosilane (TMCS), and trimethylsilylimidazole (TMSI) to be analyzed for levoglucosan, abietic and dehydroabietic acid. Derivatization was necessary in order to convert the polar O-H groups to relatively nonpolar groups, resulting in more volatile compounds for analysis on the GC/MS (Bergauff, Ward et al. 2009).

Eight of the remaining filter halves were then selected for highest collected mass (four from each stove type) and analyzed for PAHs. Extraction glassware (Figure 4) was cleaned and sterilized as outlined in EPA Method TO-13A 6.2.2. Filters were spiked with 20 μL of internal reference standard (EPA 525.5 mix) diluted to 50 $\text{ng}/\mu\text{L}$ at least one hour prior to extraction. The lower reservoir was placed in a heating mantle and set to 40% power at 120 V to obtain a rate of three cycles per hour and the water-cooler condenser was connected to bench cold water and set to a continuous stream. A solvent of approximately 700mL of 10% diethyl ether in hexane was added to the lower reservoir and a two hour pre-extraction was completed to act as a sample blank. The extract solvent was then transferred to a drying column and the Soxhlet apparatus was then rinsed with solvent, which was also transferred and dried, and then transferred to a Kuderna-Danish (K-D) concentrator apparatus. This was repeated with an exposed filter half for an 18 hour extraction. Samples were evaporated to 5 mL and then blown down to 1 mL under a nitrogen gas stream. (EPA 1999) The extracted filter, which appeared to still retain a majority of the carbon from the sampling process, was returned to storage for possible future analysis. For all compounds, highly selective quantitation was performed using the signal for representative ions for each compound extracted from the total ion chromatogram

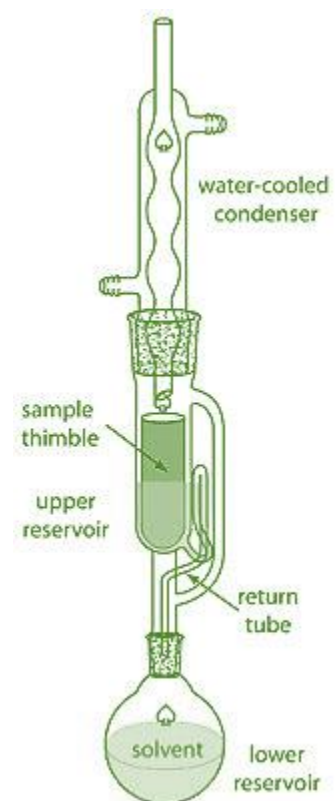


Figure 4: Soxhlet Apparatus for Continuous Extraction of PAHs

on an Agilent 6890N Gas Chromatograph with an Agilent 5973 Mass Spectrometer (GC/MS) using a Agilent Technologies HP-5 30 m column with 0.32 mm inner diameter and 0.25 μm film. (Bergauff, Ward et al. 2009).

Statistical Analysis

GC/MS data were compiled in Microsoft Excel and analyzed using R. Each data set was evaluated for the following assumptions: The two populations have normal distributions (Figure 5), meaning that the data distribution approximately follows the standard bell curve distribution in which 68% of the values are within one standard deviation of the population mean, 95% of the values lie within two standard deviations, and 99.7% are within three standard deviations, and that the data sets are sufficiently large ($n_1 = 42$ and $n_2 = 41$). The Student's t-test has another assumption that must be met; that the population variances are equal and the sample

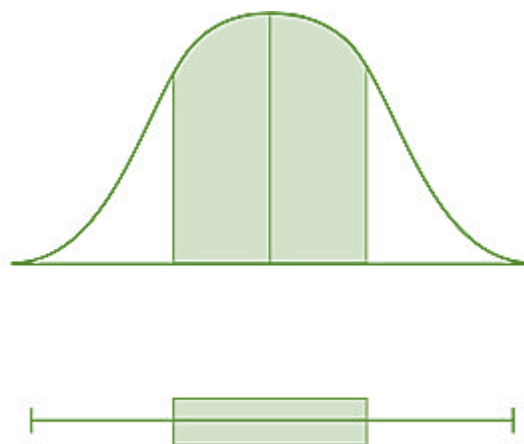


Figure 5: Boxplot vs. the standard bell curve. The interquartile range (68%) is highlighted on both visual representations.

sizes are balanced, but the Welch's t-test is more robust and the results more closely follow results for a Student's

Table 1: Summary of experimental analytes.

Analyte	Formula	MW (g/mol)	Mean _{EPA}	Mean _{TRAD}	Median _{EPA}	Median _{TRAD}	SD _{EPA}	SD _{TRAD}
Stove (Temp) Temperature	(°C)		195.3	116.2	200.6	104.4	46.1	58.8
Sample Mass (Mass)	(mg)		10.2	6.9	7.2	5.8	10.3	8.2
Levoglucozan Fraction (%) (Levo)	C ₆ H ₁₀ O ₅	162.14	9.2	9.5	9.6	10.5	4.7	3.6
Abietic Acid Fraction (%) (AA)	C ₂₀ H ₃₀ O ₂	302.46	0.045	0.136	0.021	0.106	0.073	0.130
Dehydroabietic Acid Fraction (%) (DHAA)	C ₂₀ H ₂₈ O ₂	300.44	0.753	1.427	0.602	1.020	0.611	1.275
Acenaphthene Fraction (%) (Ace)	C ₁₂ H ₁₀	154.21	0.024	0.041	0.013	0.035	0.029	0.017
Anthracene Fraction (%) (Anth)	C ₁₄ H ₁₀	178.23	0.001	0.002	0.001	0.002	0.001	0.002
Benz(a)anthracene Fraction (%) (Benz)	C ₁₈ H ₁₂	228.29	0.064	0.022	0.069	0.019	0.043	0.018
Pyrene Fraction (%) (Pyr)	C ₁₆ H ₁₀	202.25	0.010	0.004	0.008	0.004	0.010	0.002
Retene Fraction (%) (Ret)	C ₁₈ H ₁₈	234.34	0.007	0.004	0.007	0.005	0.003	0.003

t-test, even when the second assumptions of equal variance and sample size are not met. Rather than testing for the second assumption, Welch's t-test is the more powerful analytical tool in either case and can be directly applied, regardless of equal variance and sample size, so long as the normality assumption is met.

Results

Data

The data collected are outlined in Table 1, which includes the names, formula, molecular weights (MW), and statistical summaries from each stove type rather than the entire data set. This offers a general overview of the data which will be explored in more detail later in the results section.

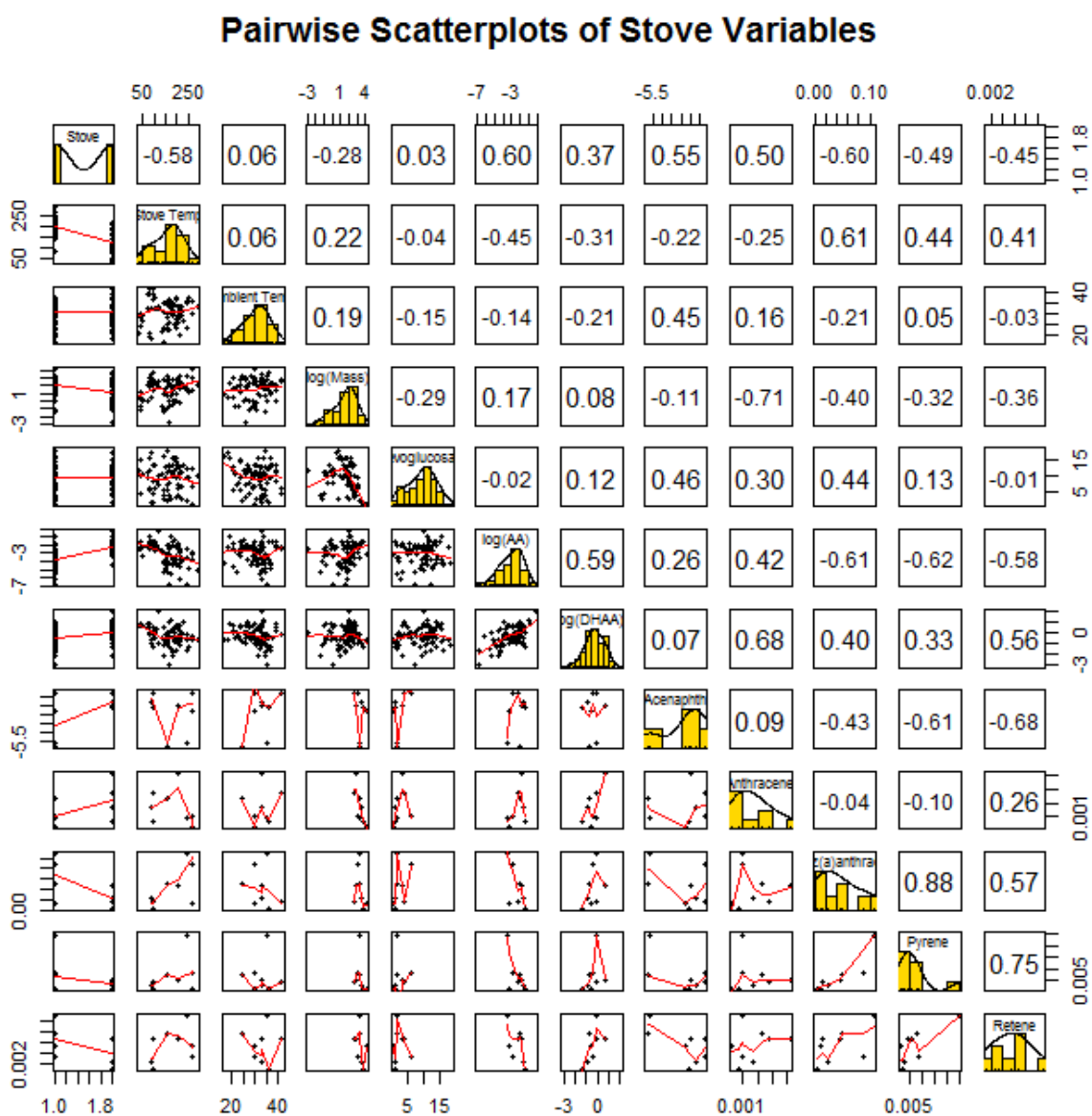


Figure 6: Pairwise scatterplot of wood stove data.

The superficial results outlined in Table 1 represent a preliminary glimpse of the data collected from the wood stove filters. Similarities between mean and median will be described and discussed in the Results and Discussion section. A detailed summary of the analytes is also included in Table 4, outlining each analyte or category of analytes and the justification for including them in the experimental analysis.

Pearson's Correlation

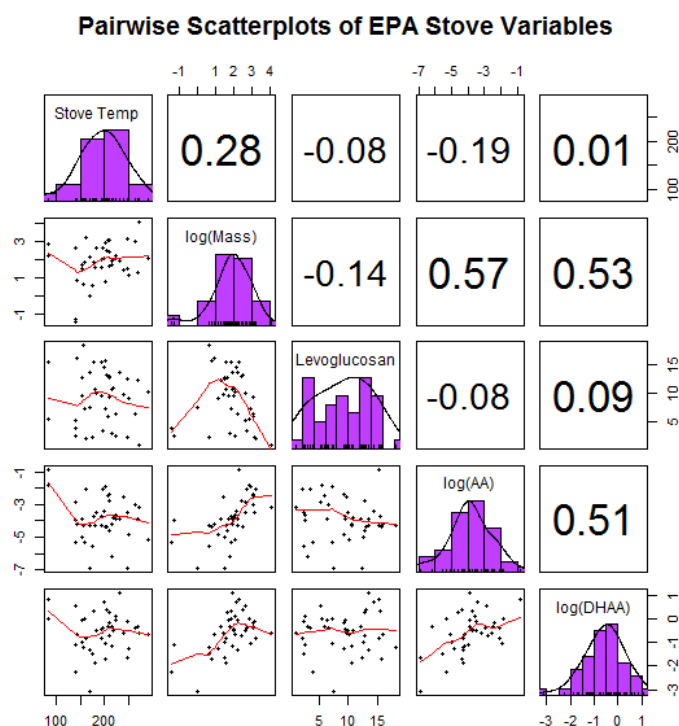


Figure 7: Pairwise scatterplot for EPA stove samples.

Notice that the Stove data in Figure 6 is a set of two separate columns because this is a binary data set with two levels, "EPA" and "Traditional". The other variables appear to follow an approximately normal distribution as they consist of continuous numerical results. The histograms labeled logAA and logDHAA appear to have two peaks in their distributions, suggesting that differences in these data could be based on stove design and should be investigated further by taking an overall look at these pairwise scatterplots separated by stove design.

A pairwise scatterplot (PS) was used in order to visually summarize the variables defined in one figure (6, 7, and 8). The PS can be especially valuable as an initial look at the total data set. The histograms on the diagonal are an overall look at how that data is distributed. The plots below the diagonal show scatterplots which indicate an overall trend of paired data sets. The numbers reported in the boxes above the diagonal are the Pearson's correlation (Pc).

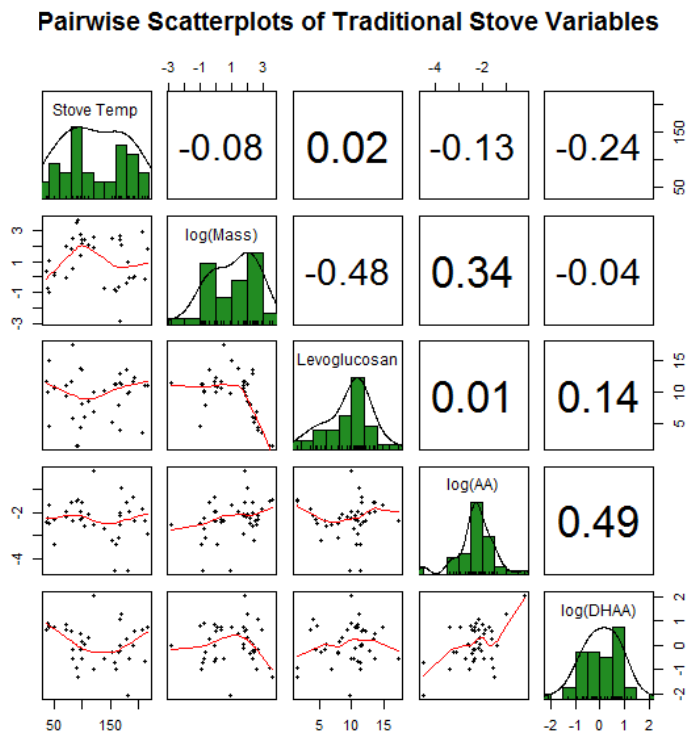


Figure 8: Pairwise scatterplot for Traditional wood stove samples.

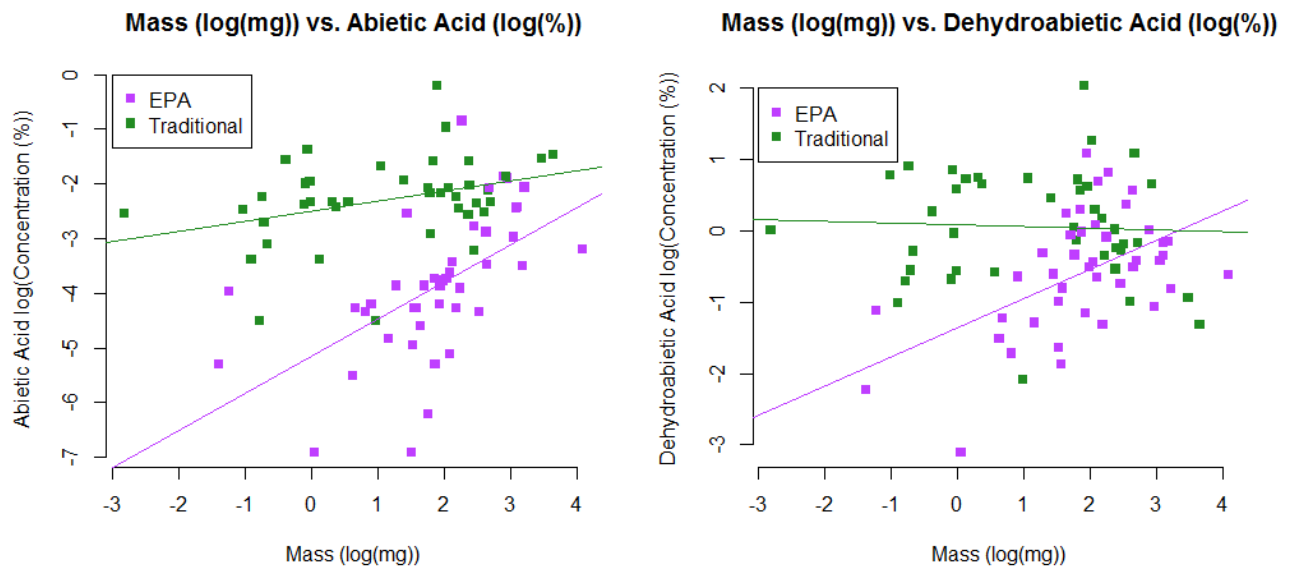


Figure 10: Scatterplot of Resin Acids by log(Mass) for EPA certified and Traditional wood stoves.

For example, Figures 7 and 8, show separated pairwise scatterplots by stove design. The PAH data have been omitted due to low sample size but will be investigated later in the results. Ambient shed temperature was also omitted because it is not directly related to any variables besides stove temperature. The P_c is a measurement of how well the data sets are related and can be easily summarized into three groups: high correlation = ± 0.5 to ± 1.0 , medium correlation = ± 0.3 to ± 0.5 , and low correlation = ± 0.1 to ± 0.3 . While the P_c is low for stove temperature in figures 7 and 8, log(Mass) appears to have high correlation to the mass fraction of both resin acids in the EPA stove and the mass fraction of levoglucosan in the traditional wood stove PS. In Figure 7 logMass vs.

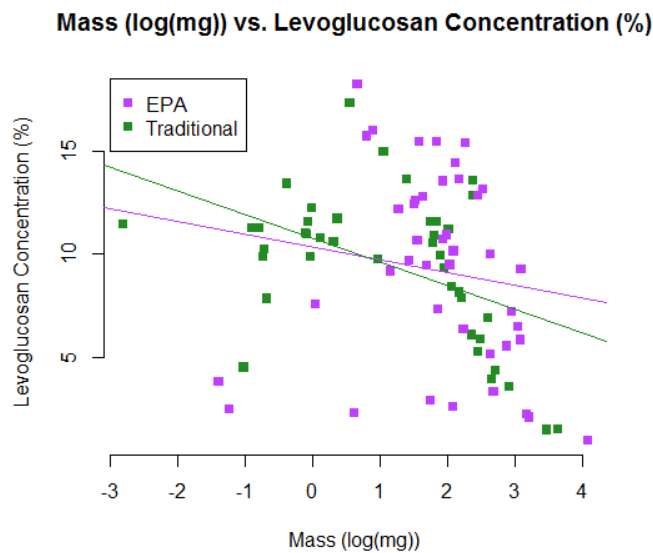


Figure 9: Scatterplot of Levoglucosan by log(Mass) for EPA certified and Traditional wood stoves.

logAA showed an upward trend for samples from the EPA stove. The relationships for these correlations are highlighted in figures 9 for resin acids and 10 for levoglucosan showing linear trends that match the highest given P_c from figures 7 and 8. These plots also show significant scatter in the data, as is expected for P_c at the low end of the “high correlation” range. Higher correlations correspond to greater slopes in the linear trend lines plotted over each scatterplot. These suggest that under conditions in which the EPA stove produces higher particulate mass, the concentration of resin acids also increases. This trend was neither as strong, nor in the same direction for both resin acids

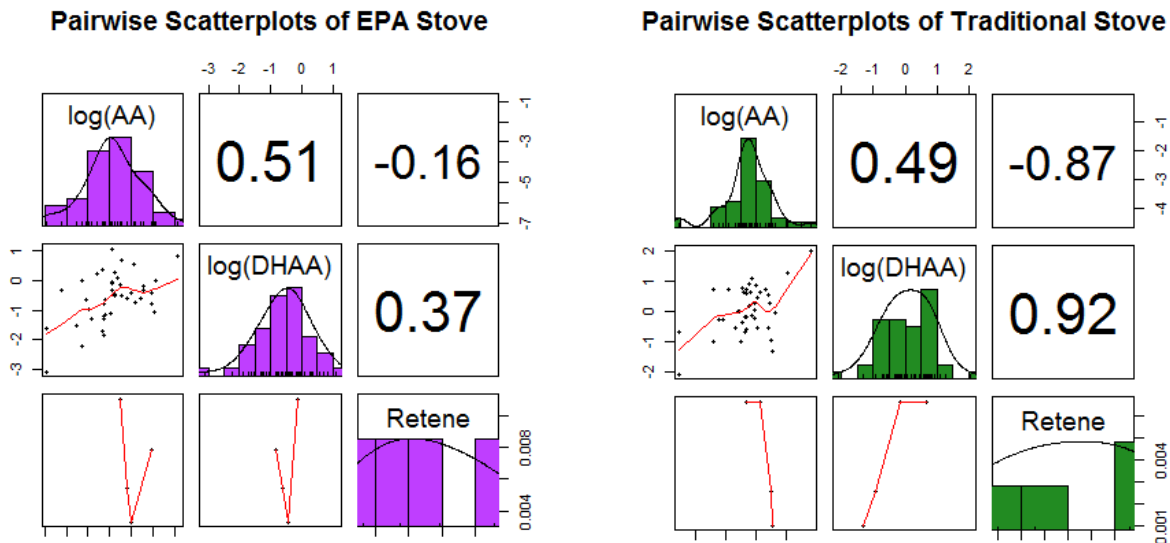


Figure 11: Scatterplots of Resin Acids by log(Mass) for EPA certified and Traditional wood stoves.

in the Traditional stove. Levoglucosan concentration decreases under conditions in which the particulate mass increases.

While this offers a plethora of information, the correlation does not distinguish independent and dependent variables, so it is still important that the relationships be investigated thoroughly. For example, the high correlation in Figure 6 between benz(a)anthracene, pyrene, and retene suggest that if you see one compound, you will most likely see the others, but not that one is causing any of the others. While this may be true, there are other high correlation values associated with the PAH variables that raise suspicion based on the low number of samples analyzed.

One PAH that does necessitate more investigation is retene in comparison to abietic acid and dehydroabietic acid. There is a moderately high correlation (Figure 11) between these three compounds, which supports the production of retene from DHAA and of DHAA from AA. More PAH samples would need to be analyzed in order to confirm this relationship.

Statistical Analyses

Based on the assumption that the data sets met the criterion of normal distribution after preliminary review of data in both box plot (Figure 12) and histogram (Figure 13) form, a Welch's two-sample t-test was applied to all of the data sets in order to determine if there was a difference in the mean values for temperature, mass, and analyte measurements. Where original data sets did not meet the criterion of normal distribution, the Welch's two-sample t-test was applied to the logarithm of the data.

Temperature

The histogram in Figure 13 illustrates the normal distribution of temperature by stove type. The same is illustrated in the side-by-side boxplots in Figure 12. To determine whether there was a statistically significant difference between the results for the two stoves, the following test was conducted in which:

μ_{EPA} = mean temperature response (°C) from the EPA stove

μ_{TRAD} = mean temperature response (°C) from the Traditional stove

1. $H_0: \mu_{EPA} - \mu_{TRAD} = 0 = D_0$ VS. $H_a: \mu_{EPA} - \mu_{TRAD} \neq 0$ or,

H_0 is the null hypothesis where no difference is observed in the mean value in temperature between stove designs,

and H_a is the alternative hypothesis suggesting a difference in those mean values.

2. Significance level: $\alpha = 0.05$ indicates that the null hypothesis will be accepted with a p-value above 0.05, and rejected if the p-value is below 0.05.

3. The test statistic (t') is the value used to determine the p-value based on the specific parameters of the data set:

$$t' = \frac{\bar{Y}_{epa} - \bar{Y}_{trad} - D_0}{\sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}}} = \frac{195.3 - 116.2 - 0}{\sqrt{\frac{46.13^2}{42} + \frac{58.85^2}{41}}} = \frac{142.3}{20.93} = 6.8$$

Stove Temperature Differences

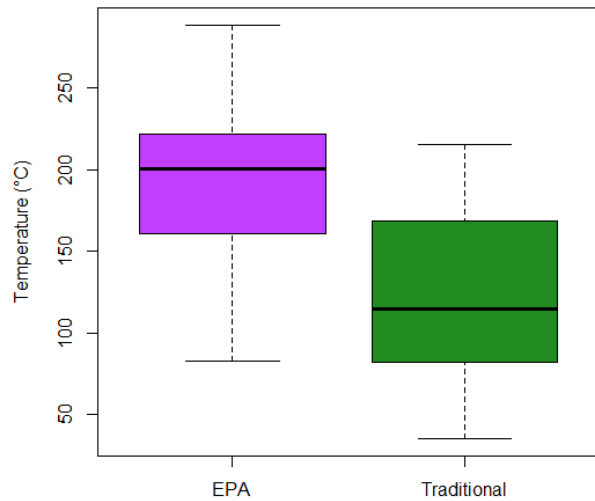


Figure 12: Side-by-side boxplot comparison of wood stove temperatures by stove design.

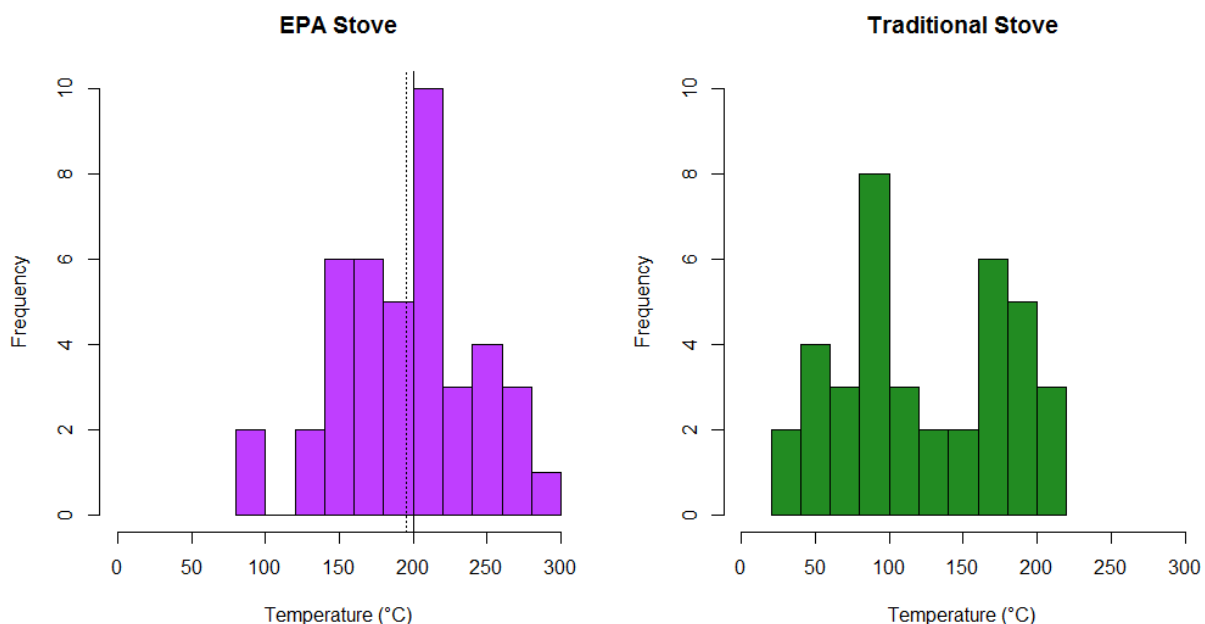


Figure 13: Histograms of temperature by stove in °C. Mean is represented by the dotted line, median is represented by the solid line.

To calculate the p-value the degrees of freedom (df) must also be calculated. Usually this is as simple as n-1, but for this experiment $n_1 \neq n_2$ and so df must be determined mathematically:

$$df = \frac{(n_{epa}-1)(n_{trad}-1)}{(n_{trad}-1)c^2 + (1-c)^2(n_{epa}-1)}, \text{ where } c = \frac{s_{epa}^2/n_{epa}}{s_{epa}^2/n_{epa} + s_{trad}^2/n_{trad}} = \frac{46.13^2/42}{46.13^2/42 + 58.85^2/41} = 0.375$$

$$\text{Therefore, } df = \frac{(42-1)(41-1)}{(41-1)0.375^2 + (1-0.375)^2(42-1)} = \frac{1640}{5.625+16.02} = 75.9 \rightarrow 76$$

Degrees of Freedom (df) are rounded up when determining $t_{\alpha/2}$ by hand, or the exact value can be used in calculating the p-value with R. In this case the p-value = 2.1e-9 and there is strong evidence that the mean stove temperature of the EPA stove is significantly different than the Traditional stove.

4. A 95% confidence interval for $\mu_{EPA} - \mu_{TRAD}$ is given as:

$$\alpha = 0.05 \Rightarrow \alpha/2 = 0.025 \Rightarrow t_{\alpha/2} \text{ for } 76 \text{ df} \Rightarrow 1.990$$

$$(\bar{Y}_1 - \bar{Y}_2) \pm t_{0.025}(\text{df}) * \sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}} = (195.3 - 116.2) \pm 1.990 * \sqrt{\frac{46.13^2}{42} + \frac{58.85^2}{41}} = 79.1 \pm 23.2 = (55.9, 102)$$

We are 95% confident that the mean temperature difference for the EPA stove vs. the Traditional woodstove is between 55.9°C and 102°C, showing that the EPA stove operates at a much higher temperature than the traditional woodstove.

The four steps statistical test is also possible in R using the following command: `t.test(Temp ~ Stove)`, and which returns the following result:

```
> t.test(Temp ~ Stove)

Welch Two Sample t-test
data: Temp by Stove
t = 6.801, df = 75.778, p-value = 2.1e-09
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
 55.9169      102.2248
sample estimates:
mean in group EPA      mean in group Traditional
195.2952                116.2244
```

Mass

The top two histograms for particulate mass from each stove in Figure 15, as well as the side by side box plot for the original data in Figure 14, illustrate that the data sets for both stove types are not normally distributed. In this case a logarithmic transformation was applied to the data and the same t-test can be conducted as follows:

$\mu_{EPA} = \log(\text{mean})$ particulate mass from the EPA stove

$\mu_{TRAD} = \log(\text{mean})$ particulate mass from the Traditional stove

1. $H_0: \mu_{EPA} - \mu_{TRAD} = 0 = D_0$ vs. $H_a: \mu_{EPA} - \mu_{TRAD} \neq 0$
2. Significance level: $\alpha = 0.05$

$$3. \quad \text{Test statistic : } t' = \frac{\bar{Y}_{epa} - \bar{Y}_{trad} - D_0}{\sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}}} = \frac{1.876 - 1.127 - 0}{\sqrt{\frac{1.087^2}{42} + \frac{1.479^2}{41}}} = \frac{0.749}{0.285} = 2.6$$

To calculate the p-value: $df = 73.4 \rightarrow 74$

Using R, this test p-value = 0.011 < 0.05 and there is moderate evidence that the log(mean) stove particulate mass of the EPA stove is different than that of the Traditional stove. This may seem unlikely when looking at the side-by-side boxplots, but take into consideration that the log transformation weighs the data more deliberately by the median than the mean, and the assumption of normality is very broadly interpreted. The data are “approximately normal”, which still satisfies that assumption.

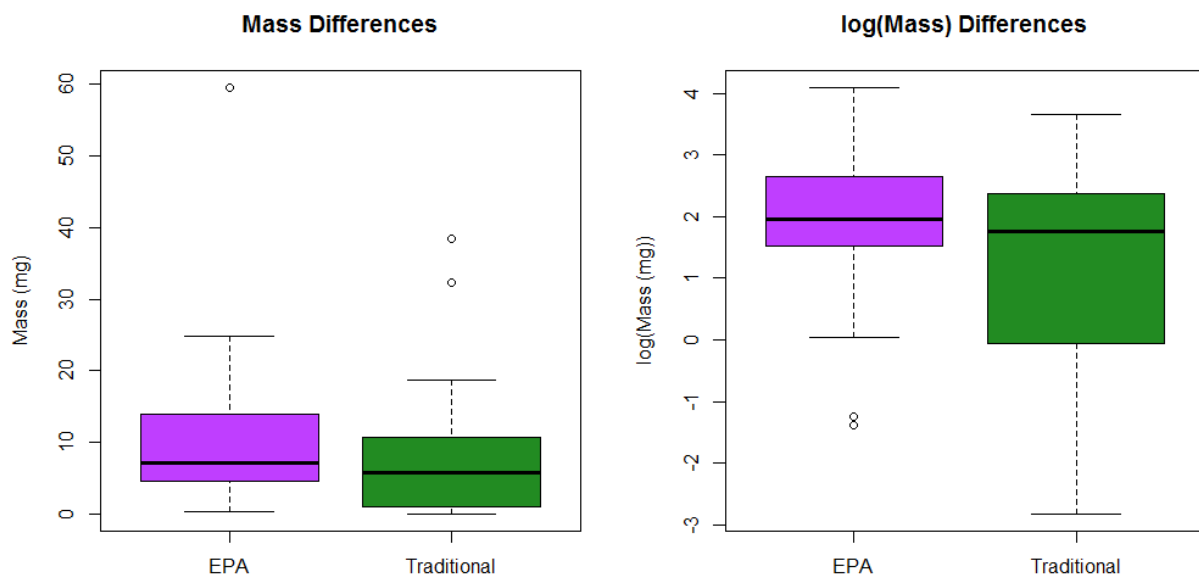


Figure 14: Side-by-side boxplots of sample mass data by stove design. The boxplot on the left are from the raw data, while those on the right have been log transformed. Open circles denote outliers as identified by R.

4. A 95% confidence interval for $\mu_{EPA} - \mu_{TRAD}$ is given as:

$$\alpha = 0.05 \Rightarrow \alpha/2 = 0.025 \Rightarrow t_{\alpha/2} \text{ for } 74 \text{ df} \Rightarrow 1.990$$

$$(\bar{Y}_1 - \bar{Y}_2) \pm t_{0.025} (df) * \sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}} = (1.876 - 1.127) \pm 1.990 * \sqrt{\frac{1.087^2}{42} + \frac{1.479^2}{41}} = 0.749 \pm 0.568 = (0.180, 1.32)$$

We are 95% confident that the log(mean) particulate mass difference for the EPA stove vs. the Traditional woodstove is between 0.180 mg and 1.32 mg, showing that the EPA stove have more particulate mass than the traditional woodstove samples.

The same test conducted in R using the following command: `t.test(log(Mass) ~ Stove)`, returns the following result:

```
Welch Two Sample t-test
data: log(Mass) by Stove
t = 2.624, df = 73.402, p-value = 0.01057
```

alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 0.1801333 1.3175776
 sample estimates:
 mean in group EPA mean in group Traditional
 1.876057 1.127201

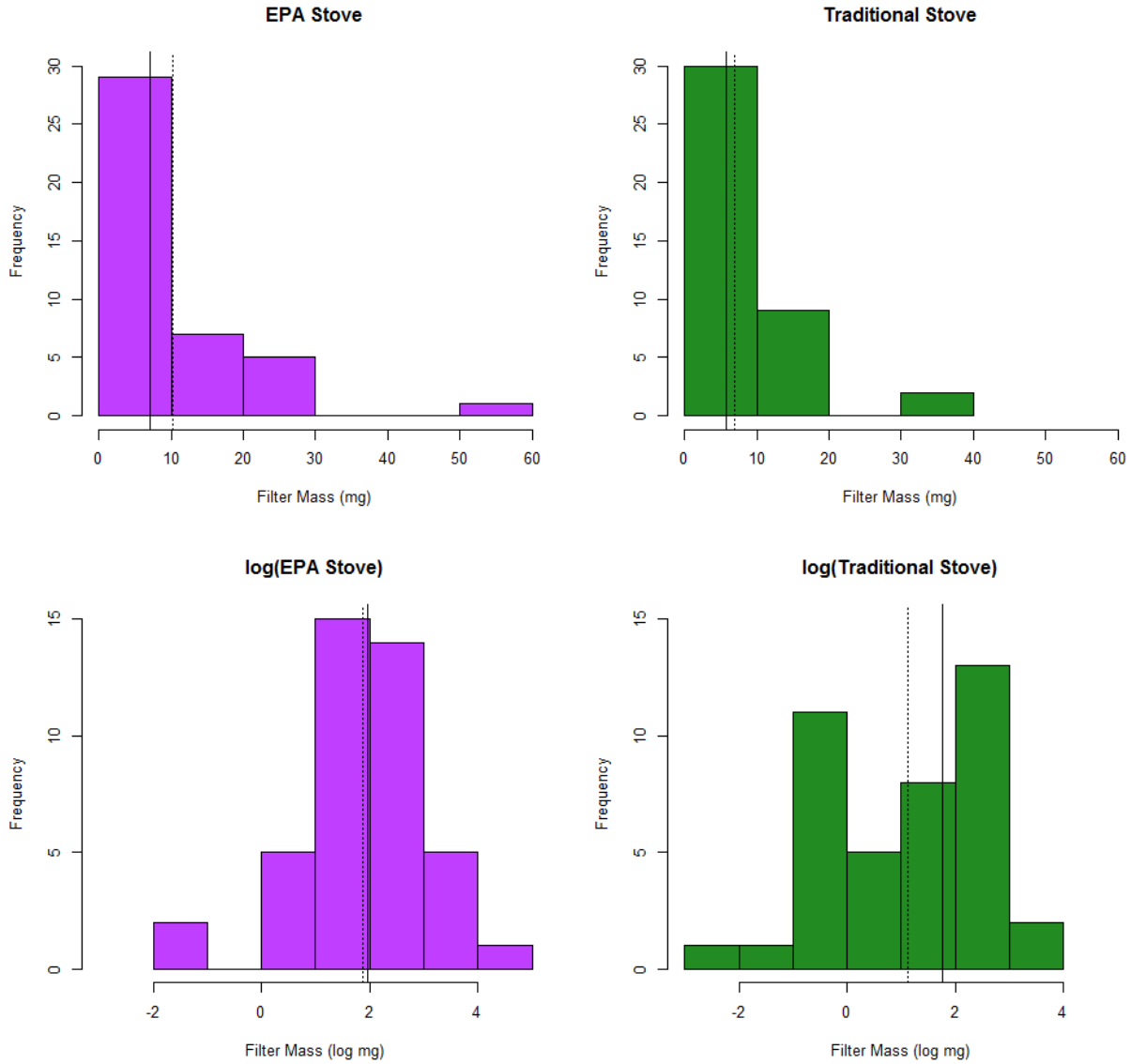


Figure 15: Histograms of sample mass data by stove type. The top set is from the raw experimental data and the lower set has been log-transformed.

Levoglucosan

The data for mean percent (%) levoglucosan (calculated as mass levoglucosan/total mass of PM_{2.5}*100) is

represented in Figures 16 and 17 as normally distributed and are thus tested as follows:

μ_{EPA} = mean percent (%) Levoglucosan from the EPA stove

μ_{TRAD} = mean percent (%) Levoglucosan from the Traditional stove

1. $H_0: \mu_{EPA} - \mu_{TRAD} = 0 = D_0$ vs. $H_a: \mu_{EPA} - \mu_{TRAD} \neq 0$
2. Significance level: $\alpha = 0.05$
3. Test statistic : $t' = \frac{9.208 - 9.477 - 0}{\sqrt{\frac{4.710^2}{42} + \frac{3.558^2}{41}}} = \frac{-0.269}{0.915} = -0.29$
4. $df = 76.2 \rightarrow 77$

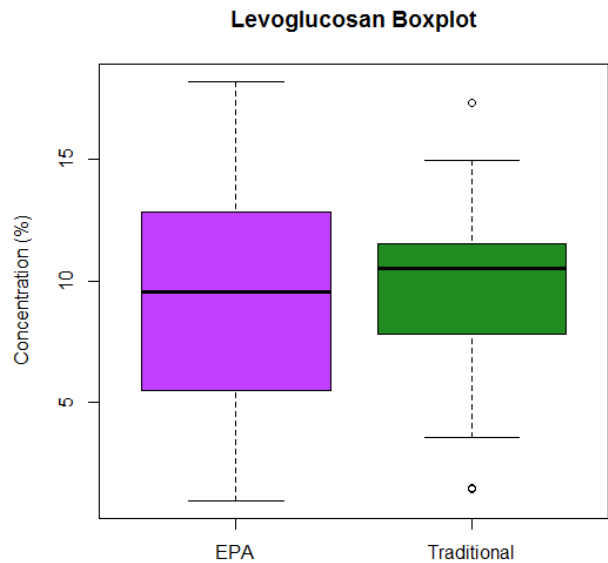


Figure 16: Side-by-side boxplots of % Levoglucosan by stove design

The p-value = 0.78 and there is strong evidence of little or no difference in the mean percent levoglucosan of the EPA and Traditional woodstoves. The conclusion is stated in this manner because the p-value is always in support of the null hypothesis.

This four step statistical test is also possible in R using the following command: `t.test(Levo ~ Stove)`, and returns the following result:

Welch Two Sample t-test
data: Levo by Stove

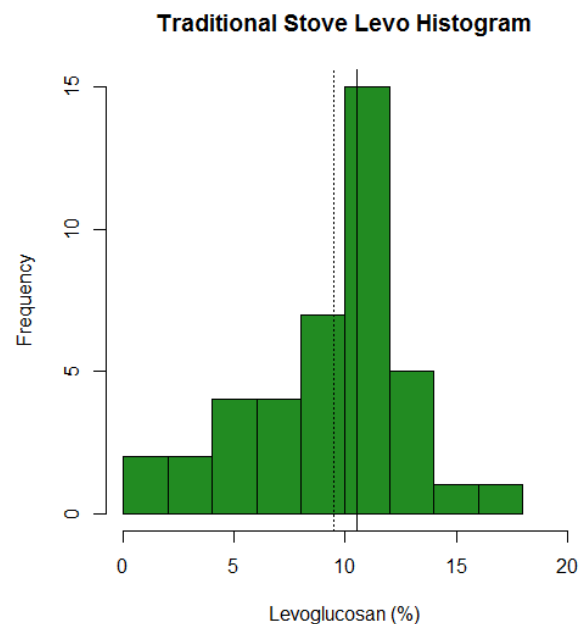
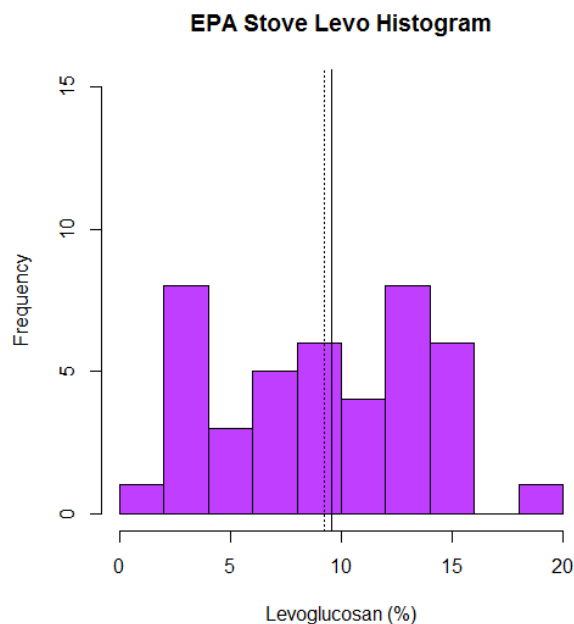


Figure 17: Histograms for % Levoglucosan by stove design.

t = -0.2944, df = 76.235, p-value = 0.7692
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -2.091340 1.552627
 sample estimates:
 mean in group EPA mean in group Traditional
 9.207619 9.476976

Given that there is no difference in the means, the true mean for levoglucosan must be determined. A one-sample t-test can be run depending on if the data pass four assumptions.

1. The dependent variable is measured on a continuous scale.
2. The data are independent of one another (one result does not influence another).
3. There are no significant outliers (see Figure 16).
4. The dependent variable is approximately normally distributed (see Figures 16 and 17)

Having met these assumptions the test was conducted in R with the following results:

```
> t.test(Levo)
One Sample t-test
data: Levo
t = 20.4681, df = 82, p-value < 2.2e-16
alternative hypothesis: true mean is not equal to 0
95 percent confidence interval:
 8.432842            10.248508
sample estimates:
mean of x = 9.340675
```

Therefore, the mean fraction of levoglucosan in the PM_{2.5} from these stoves is between 8.4% and 10.2%.

Abietic Acid

The two histograms for abietic acid (AA) from each stove in Figures 18 and 19 illustrate that the data sets for both stove types are not normally distributed. In this case a logarithmic transformation was applied to the data and the same t-test can be conducted as follows:

$\mu_{EPA} = \log(\text{mean percent (\% AA from the EPA stove)})$

$\mu_{TRAD} = \log(\text{mean percent (\% AA from the Traditional stove)})$

1. $H_0: \mu_{EPA} - \mu_{TRAD} = 0 = D_0$ vs. $H_a: \mu_{EPA} - \mu_{TRAD} \neq 0$
2. Significance level: $\alpha = 0.05$
3. Test statistic : $t' = \frac{\bar{Y}_{epa} - \bar{Y}_{trad} - D_0}{\sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}}} = \frac{-3.871 - (-2.284) - 0}{\sqrt{\frac{1.303^2}{42} + \frac{0.7972^2}{41}}} = \frac{-1.587}{0.2365} = -6.711, \quad df = 68.2 \rightarrow 69$

Using R, this test p-value = 4.7e-9 << 0.05 and there is strong evidence that the log(mean) stove abietic acid mass fraction of the EPA stove is significantly different than that of the Traditional stove.

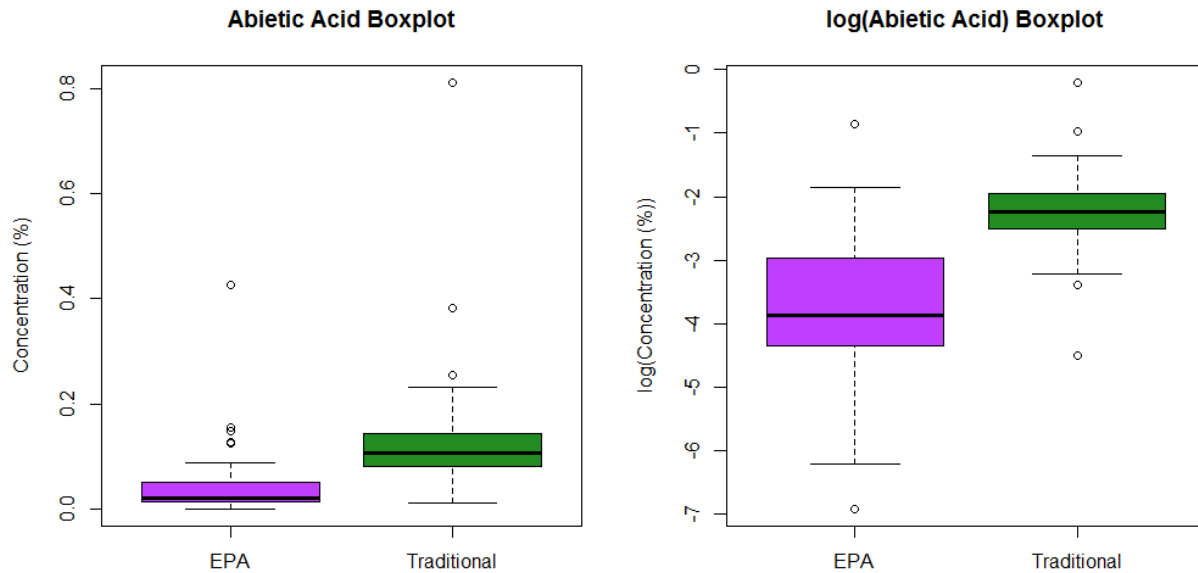


Figure 18: Side-by-side boxplots of % Abietic Acid by stove design. The boxplot on the left is from the raw data, while those on the right have been log transformed.

4. A 95% confidence interval: $t_{\alpha/2}$ for 69 df => 1.994

$$95\% \text{ CI} = (-3.871 - (-2.284)) \pm 1.994 * \sqrt{\frac{1.303}{42} + \frac{0.7972^2}{41}} = -1.587 \pm 0.472 = (-2.06, -1.12)$$

We are 95% confident that the log(mean) percent (%) AA difference for the EPA stove vs. the Traditional woodstove is between -2.06 log(mg) and -1.12 log(mg), showing that the EPA stove produces particulate with lower abietic acid mass fraction than the traditional woodstove.

The same test conducted in R using the following command: `t.test(log(AA) ~ Stove)`, returns the following result:

```

Welch Two Sample t-test
data: log(AA) by Stove
t = -6.7079, df = 68.185, p-value = 4.695e-09
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-2.058399          -1.114551
sample estimates:
mean in group EPA      mean in group Traditional
-3.870504              -2.284029

```

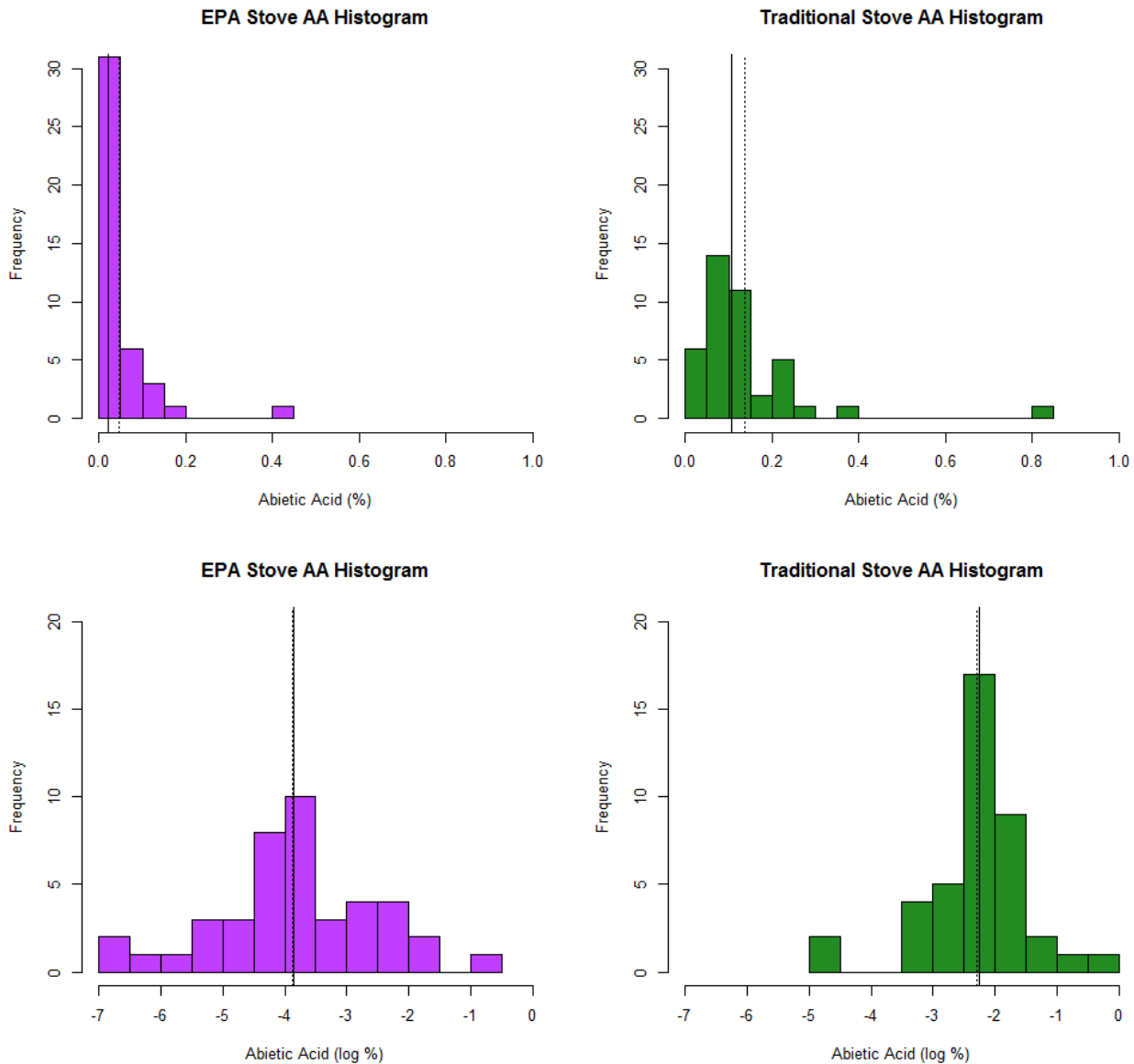


Figure 19: Histograms of % Abietic Acid by stove type. The top set is from the raw data and the lower set is log-transformed.

Dehydroabietic Acid

The raw data box plots and histograms for dehydroabietic acid (DHAA) from each stove in Figures 20 and 21 illustrate that the data sets for both stove types are not normally distributed. In this case a logarithmic transformation was applied to the data and the same t-test can be conducted as follows:

$$\mu_{\text{EPA}} = \log(\text{mean percent (\% DHAA from the EPA stove)})$$

$$\mu_{\text{TRAD}} = \log(\text{mean percent (\% DHAA from the Traditional stove)})$$

1. $H_0: \mu_{\text{EPA}} - \mu_{\text{TRAD}} = 0 = D_0$ vs. $H_a: \mu_{\text{EPA}} - \mu_{\text{TRAD}} \neq 0$

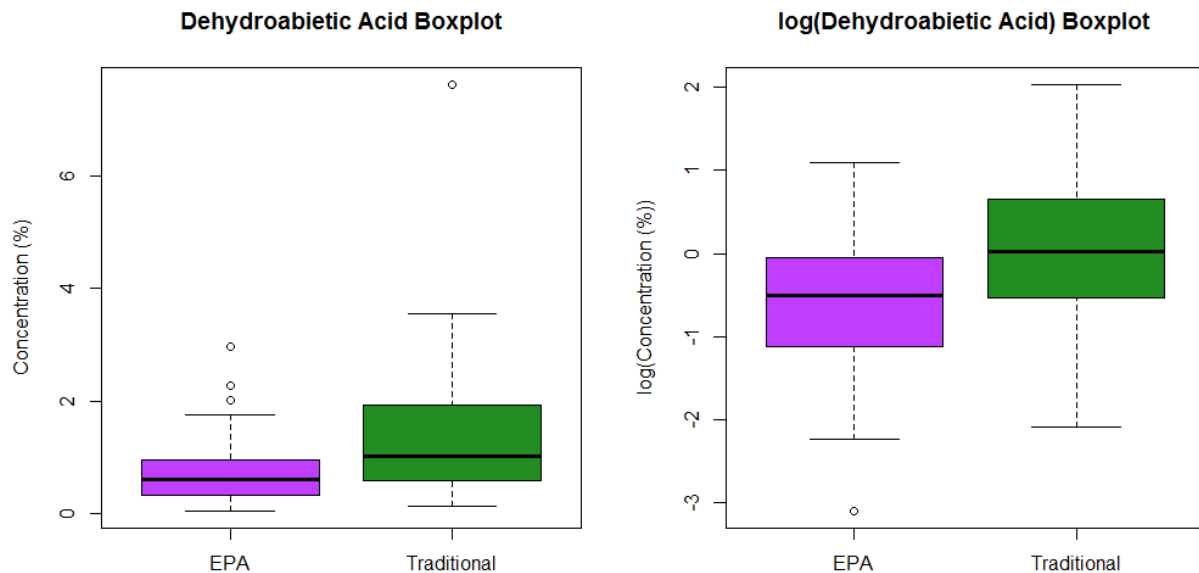


Figure 20: Side-by-side boxplots of % Dehydroabietic Acid by stove design. The boxplot on the left are from the raw data, while those on the right have been log transformed.

2. Significance level: $\alpha = 0.05$

3. Test statistic : $t' = \frac{\bar{Y}_{epa} - \bar{Y}_{trad} - D_0}{\sqrt{\frac{s_{epa}^2}{n_{epa}} + \frac{s_{trad}^2}{n_{trad}}}} = \frac{-0.5882 - 0.06225 - 0}{\sqrt{\frac{0.8403^2}{42} + \frac{0.7894^2}{41}}} = \frac{-0.6505}{0.1789} = -3.6, \quad df = 80.9 \rightarrow 81$

Using R, the p-value = $4.86e-4 < 0.05$ and there is strong evidence that the log(mean) percent (%) DHAA of the EPA stove is different than that of the Traditional stove.

4. 95% CI = $(-0.588 - 0.063) \pm 1.987 * \sqrt{\frac{0.8403^2}{42} + \frac{0.7894^2}{41}} = -0.651 \pm 0.356 = (-1.01, -0.30)$

We are 95% confident that the log(mean) percent (%) DHAA difference for the EPA stove vs. the Traditional woodstove is between -1.01 log(mg) and -0.30 log(mg), showing that the EPA stove produces particulate with lower mass fraction dehydroabietic acid than the traditional woodstove. The same test conducted in R using the following command: `t.test(log(DHAA) ~ Stove)`, returns the following result:

```
Welch Two Sample t-test
data: log(DHAA) by Stove
t = -3.6356, df = 80.883, p-value = 0.0004862
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-1.0064758      -0.2944752
sample estimates:
mean in group EPA      mean in group Traditional
-0.58822203           0.06225345
```

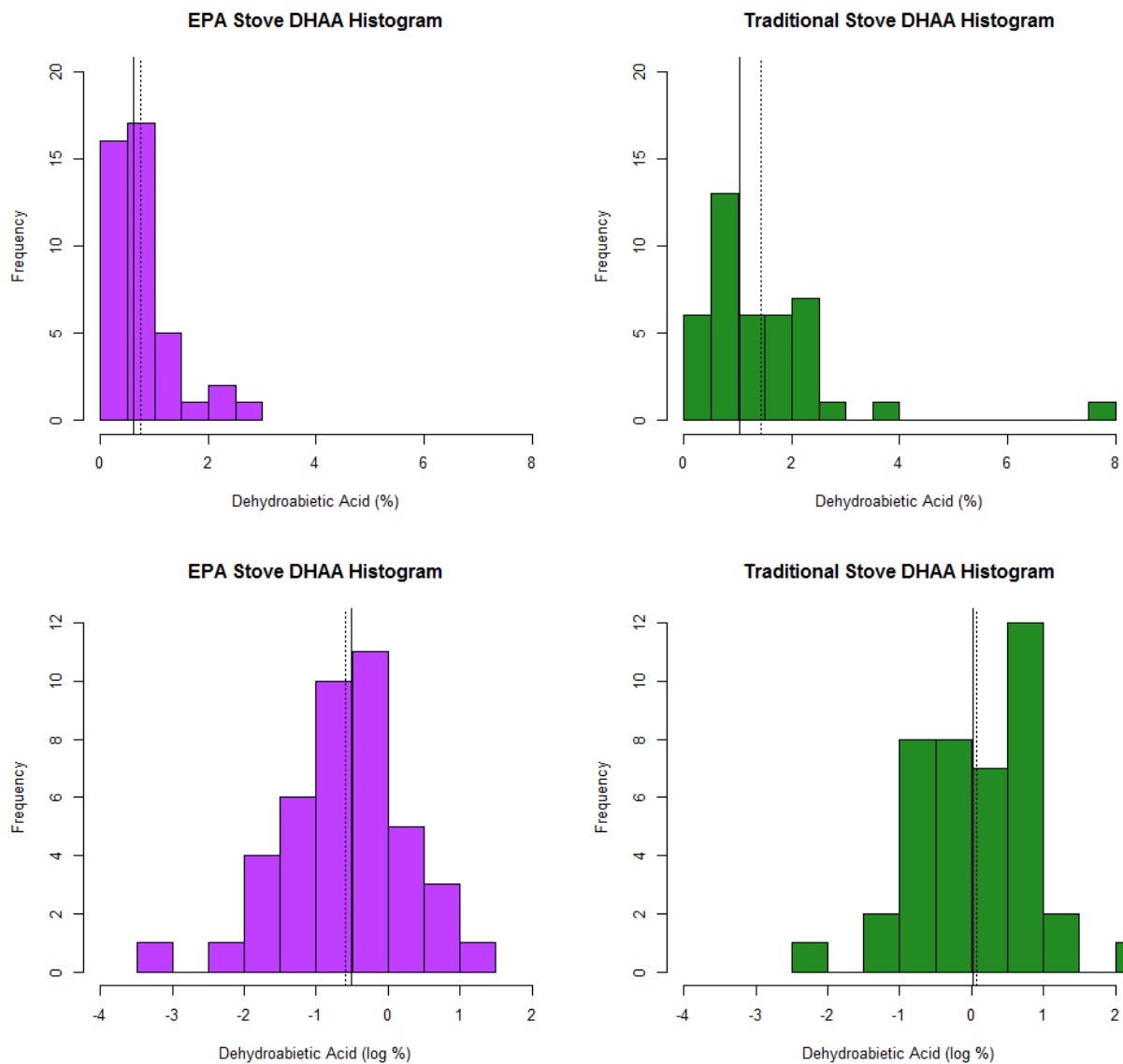


Figure 21: Histograms of % Dehydroabietic Acid by stove type. The top set is from the raw data and the lower set is log-transformed.

Table 2: Summary of statistical data for Temp, log(Mass), Levo, log(AA), and log(DHAA).

PAH	Temperature (°C)	log(Mass) (mg)	Levoglucosan (%)	log(Abietic Acid) (%)	log(Dehydroabietic Acid) (%)
t'-statistic	6.8	2.6	-0.29	-6.71	-3.64
df	75.8	73.4	76.2	68.2	80.9
p-value	2.1e-09	0.011	0.78	4.7e-09	4.9e-04
95% CI	55.9 to 102	0.18 to 1.32	-2.09 to 1.55	-2.06 to -1.12	-1.01 to -0.30

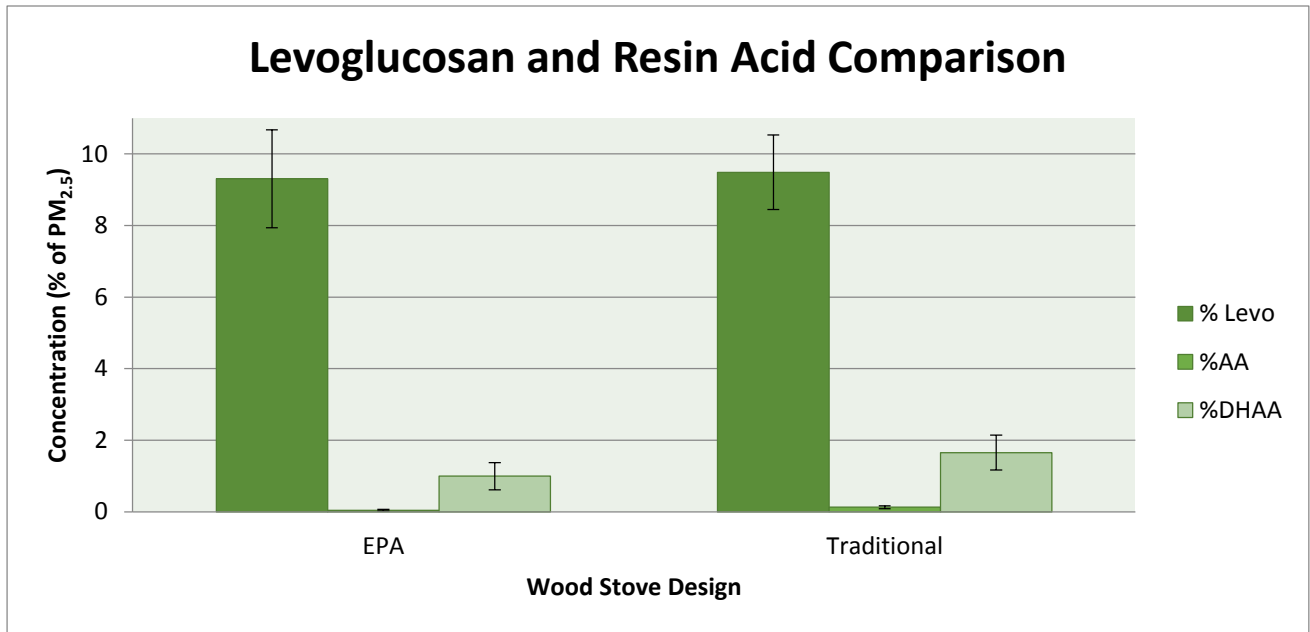


Figure 22: Side-by-side bar plot comparison of levoglucosan (Levo), abietic acid (AA), and dehydroabietic acid (DHAA).

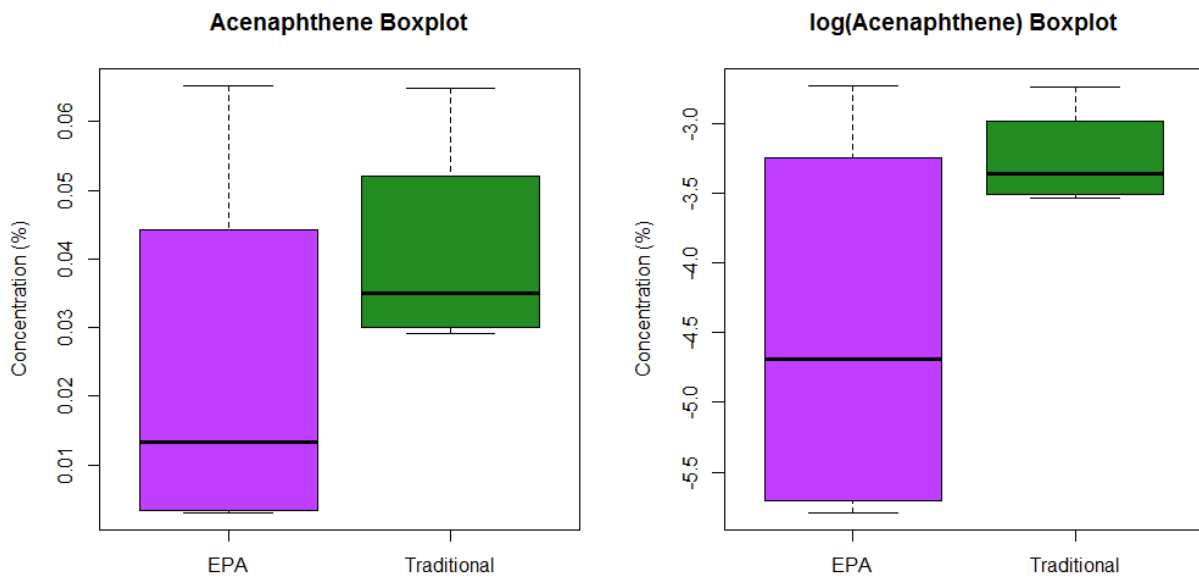


Figure 23: Side-by-side boxplots of Acenaphthene and log(Acenaphthene) data by stove design.

Polycyclic Aromatic Hydrocarbons

Because of the time and cost of the analyses, the PAH content of particulate matter generated by the two stoves was measured from a limited number of samples ($n_{EPA} = 4$ and $n_{TRAD} = 4$). Figure 27 shows the mass fractions of five prominent PAHs in particulate from the EPA and traditional wood stoves. Using side-by-side

comparisons of the PAH data, as seen in Figures 23, 24, and 25, the original information for acenaphthene is skewed to the right, necessitating a log transformation, similar to the transformations used in the mass, AA, and DHAA results. This creates a distribution that is approximately normal, improving the reliability of any test results and satisfying the assumptions of the t-test.

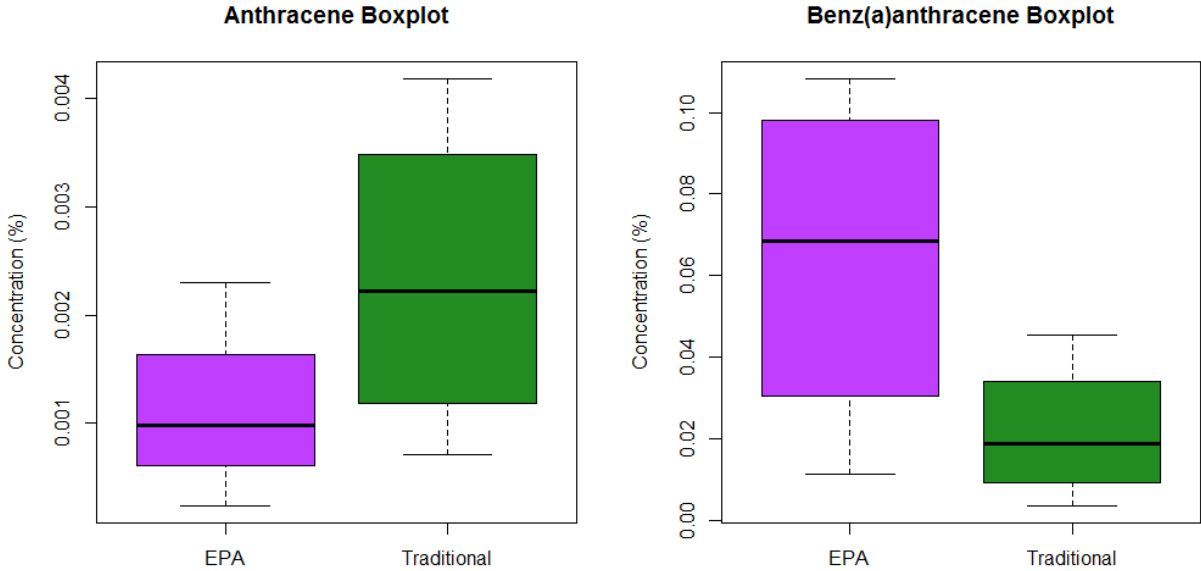


Figure 24: Side-by-side boxplots of Anthracene and Benz(a)anthracene by stove design.

The boxplots in Figure 24 appear approximately normal for both anthracene and benz(a)anthracene in their distribution, which is encouraging given that there are only four data points per stove.

Finally, a similar normality in distribution is observed for Pyrene and Retene in Figure 25.

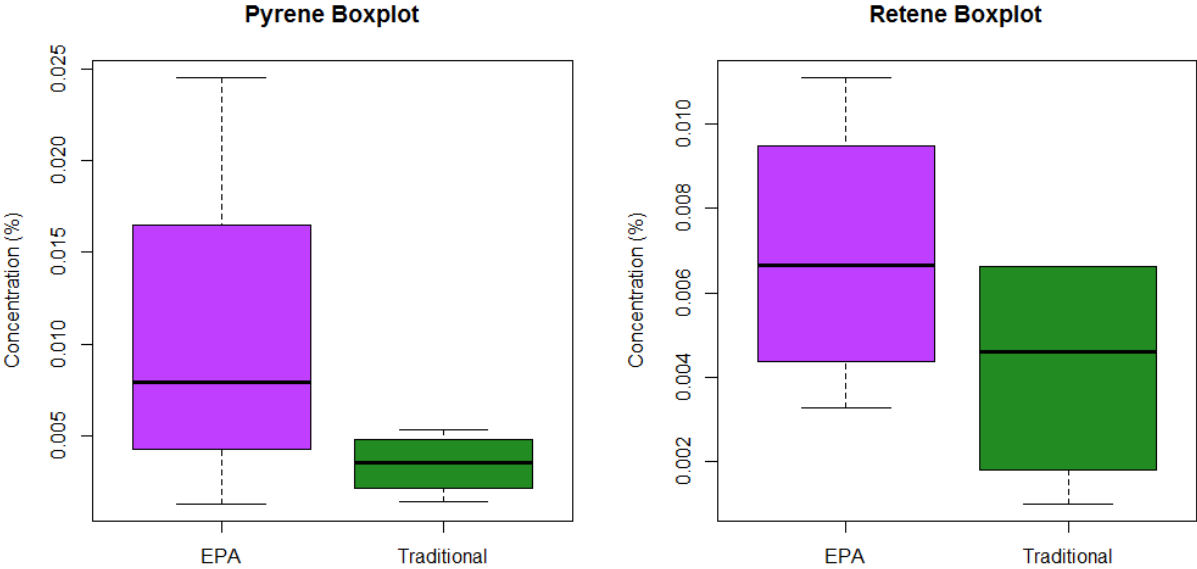


Figure 25: Side-by-side boxplots of Pyrene and Retene by stove design.

The uncertainty implied by the limited data set means that only a limited set of conclusions can be drawn from the PAH data. However, the retene results are of particular interest due to the similarity in chemical structure with the resin acids (see Table 4). Just as abietic acid is oxidized into DHAA, retene is the aromatization product of dehydroabietic acid (Simoneit, Rogge et al. 2000). Using R, the following hypothesis is tested:

μ_{EPA} = mean retene response from the EPA stove

μ_{TRAD} = mean retene response from the Traditional stove

1. $H_0: \mu_{\text{EPA}} - \mu_{\text{TRAD}} = 0 = D_0$ vs. $H_a: \mu_{\text{EPA}} - \mu_{\text{TRAD}} \neq 0$
2. Significance level: $\alpha = 0.05$

```

Welch Two Sample t-test
data: Ret by Stove
t = 1.2314, df = 5.861, p-value = 0.2653
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.002718577 0.008163119
sample estimates:
mean in group EPA      mean in group Traditional
0.006926074           0.004203803

```

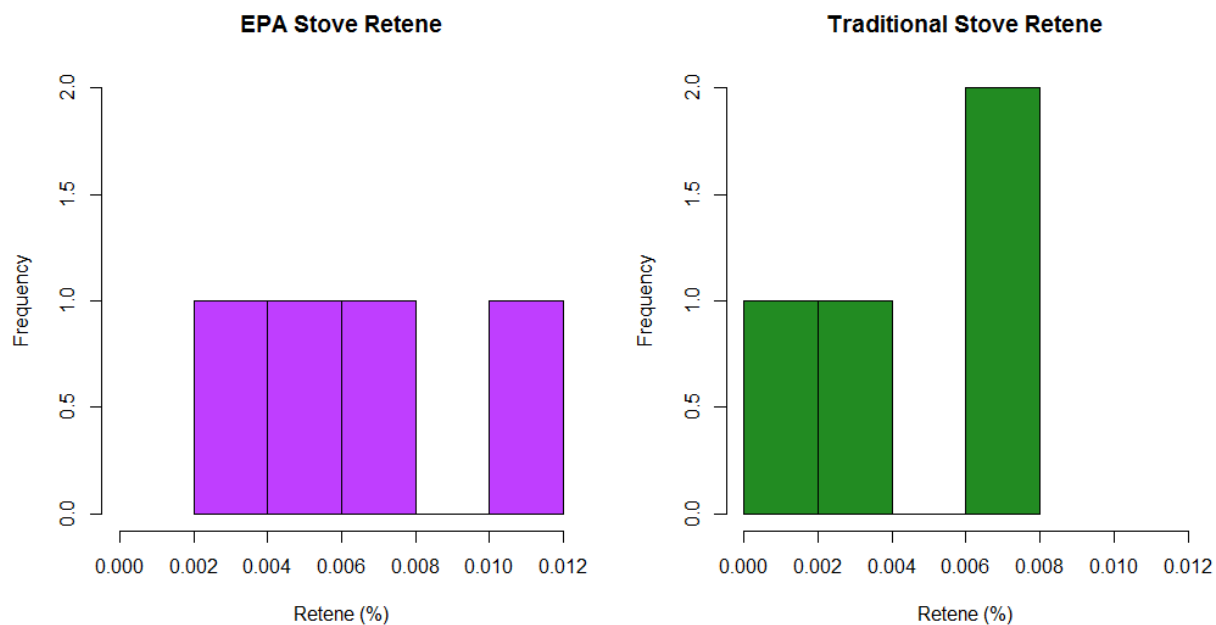


Figure 26: Histogram of % Retene by stove design.

A summary of the resulting statistics are listed in Table 3 along with the same test executed on the other PAHs. All of the p-values are greater than $\alpha = 0.05$, indicating a rejection of the null hypothesis of the Welch's t-test and conclude that no statistical differences in PAHs were observed by stove design.

Table 3: Summary of statistical data for PAHs from Welch's t-test conducted in R.

PAH	log(Acenaphthene) (%)	Anthracene (%)	Benz(a)anthracene (%)	Pyrene (%)	Retene (%)
t'-statistic	-1.6	-1.4	1.8	1.4	1.2
df	3.4	4.8	4.0	3.2	5.9
p-value	0.20	0.22	0.14	0.26	0.27
95% CI	-3.5 to 1.1	-0.0035 to 0.0010	-0.022 to 0.11	-0.0086 to 0.022	-0.0027 to 0.0082

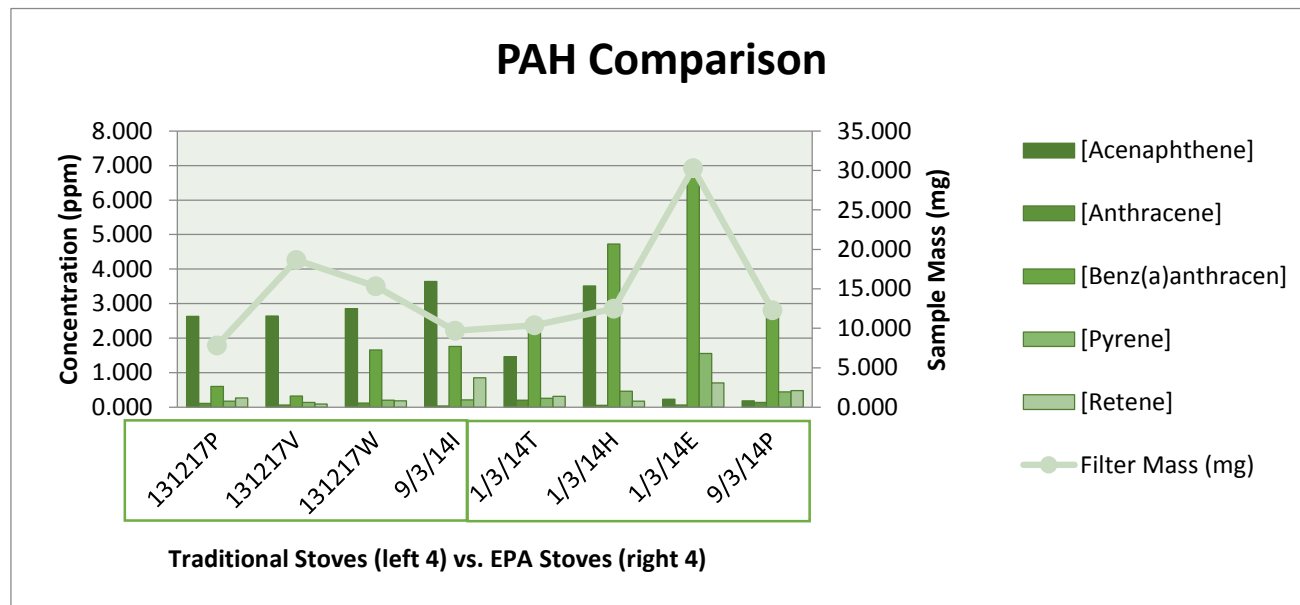


Figure 27: Side-by-side bar plot comparison of polycyclic aromatic hydrocarbons (PAHs).

Discussion

A detailed chemical and statistical analysis was completed on PM_{2.5} emissions from two wood stoves, an EPA certified and a Traditional wood stove. A sufficient number (n > 30) of samples were collected from each stove type in order to accurately reflect the sample population of woodstoves being represented. Specific chemical tracers were selected for analysis based on their importance to source apportionment (levoglucosan), adverse health effects (resin acids and PAHs), and secondary pyrolysis products (retene).

A chief motivation for this project were the results reported in "The effect of a woodstove changeout on ambient levels of PM_{2.5} and chemical tracers for woodsmoke in Libby, Montana."(Bergauff, Ward et al. 2009). As discussed earlier, their results for resin acids showed an unanticipated increase in the abietic acid levels after replacing many of the traditional combustion devices with EPA stoves and an initial increase and then a decrease in the dehydroabietic levels. The results from the current project, however, show a definite decrease in both resin acids (Figures 11, and 18-21) in the PM_{2.5} from the EPA stove vs. that from the traditional woodstove design.

From the values listed in the upper right diagonal of the Pearson's correlation in Figure 6, a strong relationship between stove type and temperature is observed (as seen in the first statistical test). Temperature

and log(mass) also appear to have some strong relationships with the PAHs. However, a Pearson's correlation of 0.88 indicates a strong correlation between two PAHs, which indicates that one PAH is resulting in the direct response of another PAH. While cause and effect are not the case, this would suggest that burn conditions that produce higher mass fractions of some PAHs also produce higher mass fractions of others, resulting in benz(a)anthracene, pyrene, and retene occur in relative quantities to one another. This is where the importance of human interpretation of the data must be observed.

The results in Figures 7 through 11 suggest that there are few significant correlations between results within a given stove type. Correlations on the low end of the "high correlation" range are observed between particulate mass and PM_{2.5} composition, suggesting that burn conditions that produce higher PM_{2.5} concentrations may also produce lower mass fractions of levoglucosan and higher mass fractions of the resin acids.

Stove temperature and percent levoglucosan were normally distributed, meeting the conditions of a Welch's t-test. However, the results for mass, abietic acid, and dehydroabietic acid were heavily skewed and a log transformation was applied, resulting in a normal distribution and report of those results in the log scale. The t-test on a very small data set yielded no differences in PAH levels between stove designs.

Temperature

The basis of many chemical differences between the EPA woodstove and traditional woodstoves are the burn conditions within each wood stove. In this study, temperature (°C) was measured for each device with each sample collected. The mean operating temperature of the EPA stove was between 55.9°C and 102.3°C higher than the Traditional stove. As increased temperature corresponds to more complete combustion and more efficient use of wood fuel, the higher operating temperatures seen in the EPA stove should have been reflected in the mass and sample composition. Essentially, while a definite difference in mean temperature between stove designs is observed, the practicality of that difference lacks in-home applicability. Higher operating temperatures would equate to higher home temperatures, so a more practical approach would involve maintaining the same operating temperature to more accurately reflect stove operations as they would be conducted in real life settings.

Mass

While the differences in the mass of PM_{2.5} from the stoves was moderate, the trend was opposite than that observed by Bergauff, Ward et al. and counterintuitive given the goals and regulations applied to modern EPA wood stove design. It is important to recognize that this study was not designed to quantify total PM_{2.5} emissions from either stove; the results presented here indicate only that the concentration of PM_{2.5} was higher in mixing chamber 2 for the EPA stove than for the traditional stove, but we did not measure or specifically control the volume fraction of total exhaust drawn into mixing chamber 2 for either stove. Bergauff, Ward et al. saw a decrease of up to 50% in the PM_{2.5} mass and a matching 50% decrease in levoglucosan concentrations. Our results showed higher relative PM_{2.5} levels collected from the EPA woodstove. The data collected in the Bergauff, Ward et

al. study from Libby, MT was based on ambient levels for a densely populated mountain valley, which reflects the total volume and concentrations of emissions and could have been impacted by the variety of heating, combustion, and fuel sources located in that municipality. However, the burn conditions of this study could have contributed to the increased mass observed on the sample filters. As stated in the discussion on temperature, conducting analysis on the stoves under conditions that yield the same stove temperatures would be advisable, as would a record of the mass of wood fuel consumed and the total volume of exhaust produced by each device.

The levoglucosan fractions and stove temperature data are plotted by sampling date in Figure 28. These plots demonstrate that there were significant difference in stove temperatures on different dates (as a result of different burn conditions and settings), but that levoglucosan fraction does not vary in any systematic way with sampling date.

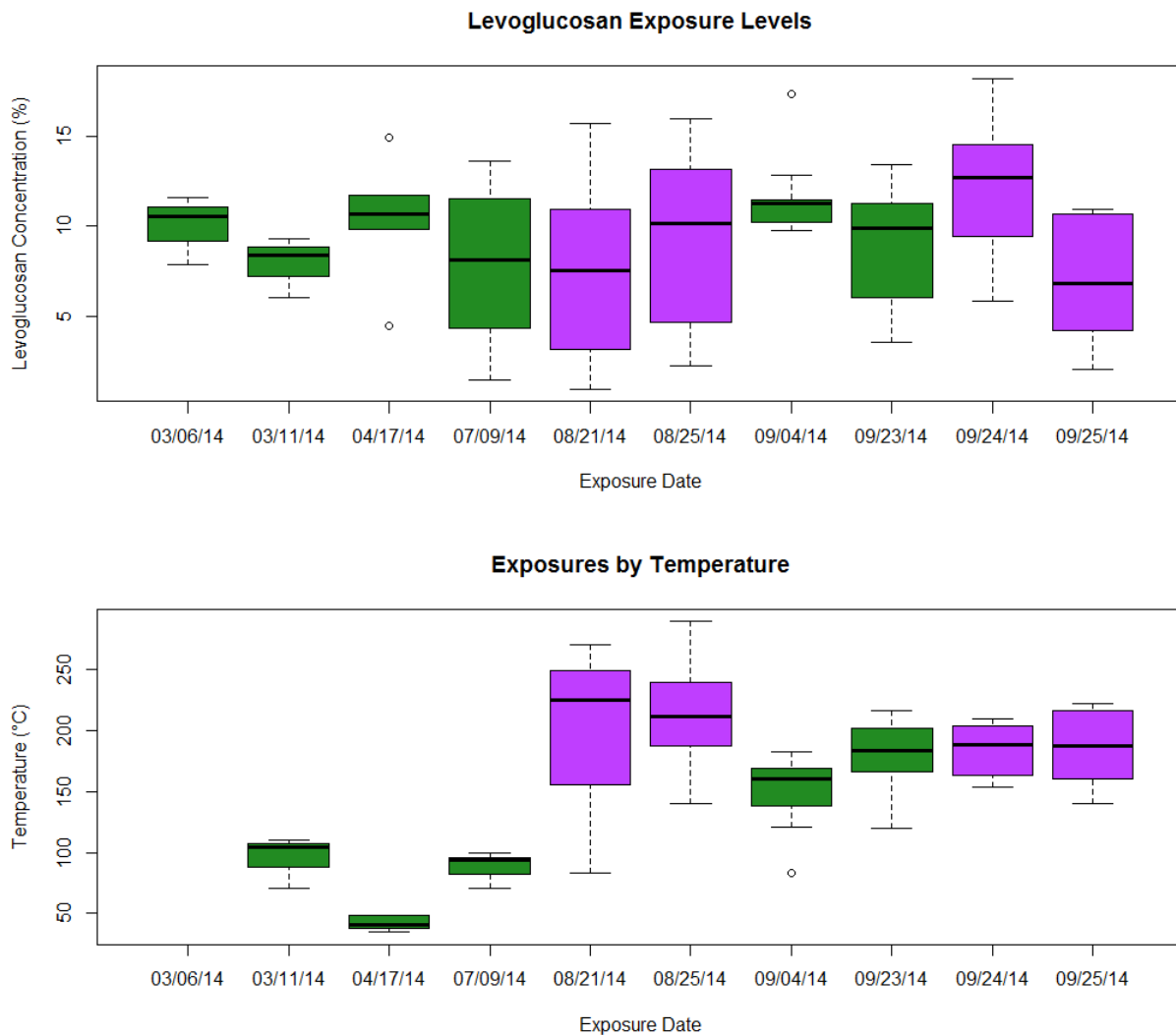


Figure 28: Temporal comparison of Levoglucosan and Temperature by sampling date.

Levoglucosan

There was no statistical difference in the reported results for levoglucosan mass fraction between wood stove designs. The similarity in mass fractions for levoglucosan between wood stove designs is encouraging as a predictive measurement in existing and future source apportionment studies. The levoglucosan results of this study suggest a similar result for conversion factor (1/mass fraction), independent of device type, between levoglucosan and wood smoke PM_{2.5} of 10.8. This conversion factor is essentially the same as, and is not significantly different from, that reported by Casseiro et al. but does have a large confidence interval. A 95% confidence interval of the true mean was assessed in a one-sample t-test to determine if the true mean value of levoglucosan was similar to a hypothetical population mean. This test indicates that the 95% confidence interval for the levoglucosan mean is between 8.43% and 10.25%, and the true conversion factor is between 9.8 and 11.9, resulting in a value very close to previously published data.

Resin Acids

The resin acid results were incredibly skewed and required a log transformation in order to be statistically analyzed for differences in stove design. As a result those findings are only valid when reported in log(mg) units. Overall, the data do support a difference in resin acid concentrations with stove design, but not one that matches those reported in previous studies. The potential health impacts resulting from increased concentrations after the Libby, MT wood stove change out program indicated an importance in focusing on the actual difference in the wood stove designs and their production of resin acids. In this study, we observed a significant decrease in resin acid production from the EPA stove vs. the Traditional wood stove, which is a logical conclusion when considering that more complete combustion occurs in the stove with higher operating temperatures. This appears to be the case and alternative explanations for the increases observed in the Libby, MT study must be explored. It has been suggested that resin acids, which are not combustion products but are emitted from the wood fuel in their native form, are released from the wood with water vapor via a process similar to steam distillation. The increased concentrations of resin acids in Libby PM_{2.5} were hypothesized to have resulted from an enhancement of this process at the higher burn temperatures typical of EPA certified stoves (Bergauff, Ward et al. 2009). A plausible explanation for the difference in the results from Libby and those in this study is that the release of the resin acids depends on the moisture content of the wood. The western larch used in the present study was well seasoned, dry (15% moisture content), and stored indoors before use.

PAHs

Comparing the PAH results in Figure 27, a visual difference is seen where Benz(a)anthracene, Pyrene, and Retene tend to be higher in the EPA stove while Acenaphthene and Anthracene tend to be higher in the Traditional woodstove, suggesting that those PAHs might appear together due to the combustion conditions of the respective stove types. Although the sample sizes are small (n_1 and $n_2 = 4$) and the histograms of these data would reveal no

additional information regarding normal distribution about these samples (Figure 26), the side-by-side boxplots indicate no serious skew and no outliers in either distribution (Figures 23-25). Hence, an appeal is made to the robustness of the t-procedures to minor departures from normality and argues that the Welch's t-test is reasonable to use and compare the mean percent PAH results between stove designs. Essentially, with the small sample size ($n = 4$), there are limited differences in PAHs vs. stove design, and it is important to emphasize that more samples are necessary to improve the reliability of any trends observed in Figures 23-26.

Unique Contribution

Using a controlled and methodical experimental design with detailed statistical analysis and one stove of each design; the findings from this study offer representative insights into the different pyrolysis conditions of each device. Working from this assumption, and comparing these results to established conversion factors from Casseiro et al, a relatively narrow window for the percent contribution of levoglucosan from total $PM_{2.5}$ generated from domestic wood stove combustion has been determined.

Critical Analysis

With regards to the experimental design, only one stove was used from each category (EPA vs. Traditional), only one fuel type was utilized, and the operating conditions for each burn were not kept consistent between runs. The variations in operating conditions were not entirely under our control, as our samples were collected when the facility was be operated for the purposes of separate studies. However, these differences were diligently recorded and analyzed in the results. This limited sample of devices and the variations in combustion conditions might detract from the overall validity of the experiment, but careful statistical analysis of the scrupulously maintained data provided a powerful tool in determining overall differences between stove designs. The complicated cleaning procedure and time consuming nature of the PAH analysis resulted in a limited number of samples for comparison, which was reflected in the results where only four filters from each stove type were used. Limited sample sizes are a specific concern in statistical analysis due to their lack of reliability in being representative of the specified population. While the statistical tests and modeling used are able to account for some of these drawbacks, there is no real substitution for a representative sample set, which would be provided if the remaining samples were to be analyzed and reported. Another drawback to the PAH analysis was the intensive reliance on solvents. Approximately two liters of hexanes mixed with 10% diethyl ether were necessary for each sample analyzed. This increased the cost and environmental impact of any large scale analysis of this type.

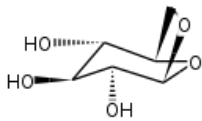
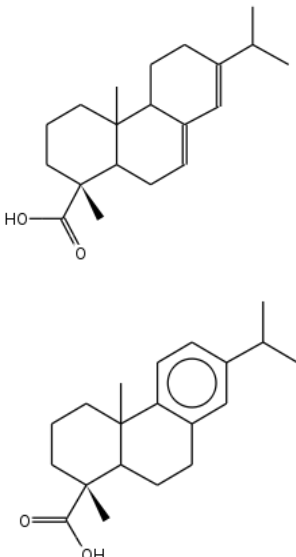
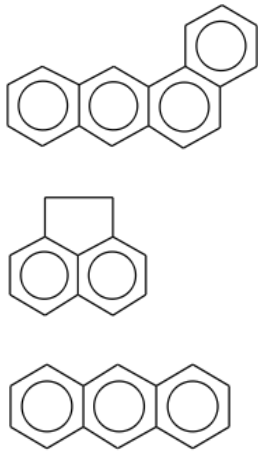
Conclusion

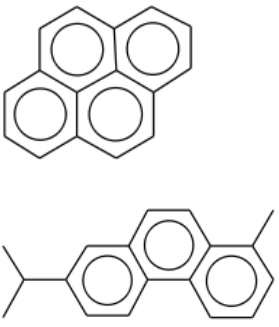
The overall question motivating this study was whether there are differences in the chemical composition of $PM_{2.5}$ resulting from use of an EPA certified wood stove vs a traditional wood stove. There is actually no 'yes' or 'no' answer to this question. While considerable differences were observed between stove types for operating temperature and resin acids, there was no difference between recorded levoglucosan levels. The resin acid results

lend evidence to suggest different chemical processes during pyrolysis, while the results observed in the levoglucosan data add to the body of evidence suggesting that levoglucosan can be used as a quantitative marker of wood smoke for source apportionment studies. Other factors such as mass and PAHs require more information to draw accurate conclusions regarding any implied differences resulting from this study. In the case of mass analysis, tighter control over the burn conditions and a measurement of total exhaust volume would add valuable information and improve comparison to certification standards. With regards to the PAH results, the remainder of our samples could be analyzed to determine preliminary trends and then repeated with future analysis. However, the cost and resource investment in the form of solvents and extraction time necessitates a cost benefit analysis of the importance of these results. The overall cost of this process could be decreased with the development of a reclamation and purification apparatus for the solvents during concentration, allowing for at least a partial recycling of purified solvent for subsequent extractions.

The results of this study lend further evidence that levoglucosan provides a suitable organic analyte for use in quantitative source apportionment. Our results indicate no significant difference in the levoglucosan mass fraction between the EPA and traditional stove. Further, although the stove designs and wood species used were different from those reported by Casseiro et al., a similar conversion factor was obtained. At the same time, these results also indicate that the resin acids are not suitable as organic markers for quantitative source apportionment, since their mass fraction is significantly different depending on stove design.

Table 4: Classification of Standards and Reagents

Class and Justification	Chemical Structure	Compound
<p>Levoglucosan is the signature chemical marker for biomass (cellulose) combustion, and mannosan and galactosan are similar sugar anhydrides associated with biomass combustion but observed at lower levels than levoglucosan.</p>		<p>Levoglucosan 99+%</p>
<p>Deuterated levoglucosan is the standard for the signature chemical marker for wood combustion</p>	<p>N/A</p>	<p>D-Levoglucosan, (D7) 98%</p>
<p>Resin Acids: Released from wood combustion with toxic effects on the liver and potential to damage DNA</p>		<p>Abietic Acid 90-95%</p> <p>Dehydroabietic Acid, technical grade</p>
<p>Deuterated resin acid standard</p>	<p>N/A</p>	<p>D-Stearic Acid, (D35) 98%</p>
<p>Derivatizing Agents</p>	<p>N/A</p>	<p>BSTFA, derivatization grade 99+%</p> <p>TMCS 97%</p> <p>TMSI, derivatization grade</p>
<p>Polycyclic Aromatic Hydrocarbons: Linked to cancer formation in lab animals and able to pass through the placental barrier.</p>		<p>1,2-Benzanthracene</p> <p>Acenaphthene</p> <p>Anthracene</p>

		<p>Pyrene</p> <p>Retene</p>
Deuterated PAH standards: Method 525.2 Internal Standard Mix	N/A	<p>Acenaphthene (D10) 97%</p> <p>Phenanthrene (D10) 99%</p> <p>Chrysene (D12) 99%</p>
Solvents	N/A	<p>Ethyl Ether, Anhydrous</p> <p>Hexanes</p> <p>Acetone</p>

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