Fairbanks, Alaska $PM_{2.5}$ Organic Composition and Source Apportionment Research Study

Final Report

August 10, 2012

by

Christopher P. Palmer, Ph.D.

The University of Montana – Missoula
Department of Chemistry and Biochemistry
Missoula, MT 59812
Office: (406) 243-4079
Fax: (406) 243-4227

1. Executive Summary

Fairbanks, AK experiences very high levels of ambient $PM_{2.5}$ during the winter months. Studies are currently under way to determine the sources of the $PM_{2.5}$ so that the issue might be addressed. Possible sources of the $PM_{2.5}$ include residential heating (wood, fuel oil, and/or natural gas combustion), transportation (diesel and gasoline engines), and coal combustion.

The current project is to provide a more complete characterization of the organic chemical composition of $PM_{2.5}$ from Fairbanks with the goal of identifying and quantifying chemical species that can be used to calculate and apportion ambient $PM_{2.5}$, particularly from wood and fossil fuel combustion.

Comprehensive chemical analyses for levoglucosan, hopanes, steranes and PAHs have been performed on up to33 ambient $PM_{2.5}$ samples from Fairbanks. Analyses have also been performed on $PM_{2.5}$ generated at OMNI scientific using representative fuels and devices. The results of these analyses have been examined with special attention to compounds reported by previous authors as emissions from wood (levoglucosan) and fossil fuel sources. Emphasis has been placed on sulfur-containing compounds (dibenzothiophene and benzonaphthothiophene) which are known emissions of diesel vehicles and were hypothesized to be markers of residential oil burners and a polynuclear aromatic hydrocarbon (picene) which has been reported as a unique marker for coal combustion. A second polynuclear aromatic hydrocarbon, bibenzyl, has been identified as a potential marker for residential oil combustion.

In general, the results show that the ambient levels of levoglucosan and selected hopanes, steranes, picene and thiophenes, measured either as a concentration in air or as a fraction of $PM_{2.5}$, are high relative to previous studies. Levoglucosan results provide a reasonable estimate of the wood smoke contribution to ambient $PM_{2.5}$, and other markers provide a sense of upper bounds for the contribution of residential oil burners and coal combustion.

Levoglucosan results indicate that wood smoke contributes 26-35% of the $PM_{2.5}$ at the State Building site, 42-62% at the North Pole site, and 20-30% at the Peger Road site. These values are significantly lower than those reported by CMB analysis and similar to somewhat lower than those determined by ^{14}C analysis. The results show that wood smoke is a substantial contributor to ambient $PM_{2.5}$. The contribution of wood smoke to ambient $PM_{2.5}$ varies substantially within a season, but has had a fairly constant seasonal average or median over the past three seasons.

Polynuclear aromatic hydrocarbon results indicate that residential oil combustion is likely a minor contributor to ambient $PM_{2.5}$ levels with a median contribution of less than 1%. Sterane analysis indicates that the upper bound for the contribution from residential oil combustion is 15%, but this is likely to be an overestimate. There is significant but unquantifiable uncertainty in these results, which rely on a single sample of no. 2 fuel oil $PM_{2.5}$.

Analysis of picene levels indicates that coal combustion also contributes a minor fraction to ambient $PM_{2.5}$ of 2.7% or less. Analysis of hopanes suggests an upper bound for coal contribution of 13%, which is likely to be an overestimate. The picene and hopane shares of coal $PM_{2.5}$ are highly variable with device, however, and the contribution of coal combustion to ambient $PM_{2.5}$ could be less than 1% from coal stoves or much higher if from HH systems.

Thiophene analysis shows that these compounds are not present in residential oil emissions, and thus cannot be used as markers of residential oil combustion. The compounds do appear in the emissions from coal combustion at shares that result in estimated coal contributions to ambient $PM_{2.5}$ of 6.7% to over 100%. It is clear from this analysis that there is another significant source of thiophenes, particularly dibenzothiophene, other than residential heating. The most likely source is transportation, since thiophenes have been reported at significant levels in diesel fuel and gasoline emissions.

2. Levoglucosan

Levoglucosan, a product of incomplete cellulose combustion, has been recognized for many years as a marker of biomass combustion in $PM_{2.5}$. In winter urban environments such as Fairbanks, this can be equated with smoke from wood-fired residential heating devices.

The University of Montana has been analyzing ambient filters from Fairbanks for levoglucosan content since beginning in the 2008-2009 heating season and continuing through the 2010-2011 heating season. Measurements have been made on over 225 filters from four separate sampling sites during that period. This report will summarize these results, providing both the raw results and interpretation of those results in terms of the fractional contribution of wood smoke to total PM in Fairbanks.

2.1 Analytical Method and Quality Control

The Fairbanks ambient $PM_{2.5}$ sampling program is described in detail in "The Fairbanks, Alaska PM2.5 Source Apportionment Research Study Final Report," July 23, 2012, by Tony Ward. Levoglucosan analyses were performed on quartz filters obtained through this sampling program as described in this report for the ^{14}C analyses.

Ambient filters received from Fairbanks are stored at -10 C until analysis is performed. Each filter is halved before analysis to allow for a second half to be archived or analyzed for ^{14}C or other analytes. The filter half was placed in a 30 mL vial and spiked with deuterated levoglucosan as in internal standard. The vials were left at room temperature to allow the standard to be absorbed onto the filter. After half an hour or until the standard solvent had evaporated, 20 mL of ethyl acetate with 3.6 mM triethylamine (TEA) was added and the samples were sonicated for half an hour to extract the desired compounds. After sonication, the filter was removed and the extract was filtered through a Whatman 0.45 µm nylon filter to remove particulates. The volume of the solvent was adjusted to 0.5 mL through evaporation under a stream of air in a sand bath at 45 °C. The sample was evaporated to dryness under a stream of air at room temperature and then derivatized with 75 µL N-*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 10 µL trimethylchlorosilane (TMCS), and 10 µL trimethylsilylimidazole (TMSI). The samples were heated in a sand bath at 70 °C for 1 hour to allow the derivatization to go to completion. Upon removal from the sand bath, the samples were diluted to 500 µL with ethyl acetate containing 3.6 mM TEA and were transferred to a GC vial for analysis.

Analysis was performed on an Agilent 6890N Gas Chromatograph with an Agilent 5973 Mass Spectrometer. An HP-5MS column ((5%-Phenyl)-methylpolysiloxane) was used with dimensions of 0.25 mm ID x 30 m length x 0.25 μm film thickness. A volume of 2 μL was injected for each analysis into a Split/Splitless FocusLiner^{TM} for HP, single taper p/w quartz wool liner. Split injection was used to analyse for levoglucosan with a split ratio of 50:1. The inlet temperature was set to 250°C and the auxiliary transfer line temperature was set at 280°C. The temperature programme was started at 40˚C for 1.5 minutes, ramped at 30°C/min to 190°C, 20°C/min to 210°C, and then 50°C/min to a final temperature of 300°C, which was held for 1.5 minutes. The mass spectrometer was operated with a solvent delay of

4.00 minutes and the mass range from 40-450 was scanned. Single ion monitoring was also used during detection. Highly selective quantitation was performed using the signal for representative ions for levoglucosan (217 m/e) and D-levoglucosan (220 m/e) extracted from the total ion chromatogram.

Calibration standards were prepared containing variable concentrations of levoglucosan and a fixed concentration of D-levoglucosan internal standard. The fixed concentration of deuterated internal standard (20 ppm) was selected to match the concentration expected from extraction of internal standard spiked on the filters, assuming 100% recovery. The standards were derivatized and analysed on the GCMS. The ratio of the peak area of levoglucosan to the peak area of D-levoglucosan standard was found for each calibration standard. A calibration curve was prepared by plotting the ratio of the two peak areas versus the concentration of the levoglucosan. Linearity was determined for each calibration curve, and all had R^2 values of at least 0.95. The concentration of levoglucosan extracted from sample filters was determined by measuring the ratio of the peak area for the analyte to that of D-levoglucosan, and reading the concentration from the calibration curve. Filter blanks and spiked filters were analysed on a regular basis, at least once for every 10 filters. Recoveries were determined for blank filters spiked with the analytes at known amounts corresponding to typical levels seen in actual sample filters. Recovery was consistently in the range of 95-105%, and blank filters did not give significant signals.

Wood smoke particulate obtained from OMNI Scientific was also analysed for levoglucosan content using essentially the same procedure. These filters had very high loads of $PM_{2.5}$, which required adaptations to the method. Smaller portions of the filters, typically 1/8 rather than ½, and extracts were often diluted before derivatization. In each case where additional dilution was necessary, the filters were spiked before extraction with sufficient deuterated levoglucosan such that the final diluted concentration would match that of other samples and standards. This ensured that the area ratios could be interpreted using the same standard curve.

In order to interpret the results for levoglucosan as a share of wood smoke $PM_{2.5}$ on the OMNI-generated filters, it was necessary to estimate the total $PM_{2.5}$. OMNI reported total $PM_{2.5}$ for quartz filter 1 (PM_{Q1}) and flow rates for quartz filters 1 (FR_{Q1}) and 2 (FR_{Q2}) for each sampling event. Quartz filter 2 was sent to UM for levoglucosan analysis. We calculated total $PM_{2.5}$ on quartz filter 2 using these data:

$$PM_{Q2} = PM_{Q1}\frac{FR_{Q2}}{FR_{Q1}}$$

This calculation assumes that the sampling time and that the $PM_{2.5}$ level in the sampling region for the two quartz filters were the same for each experiment.

2.2 Results

Raw results for all measured levoglucosan levels in ambient air (in ng/m^3) and as levoglucosan share of total $PM_{2.5}$ (in %) are provided in a spreadsheet. These data are organized by sampling site and sampling date, and total reported $PM_{2.5}$ (in µg/m^3) are also included. Based on replicate measurements, typical relative error for reported levoglucosan levels is ± 10%.

Table 1 presents averages and 95% confidence intervals for levoglucosan levels and shares by sampling site and year. Data for the RAMS site is presented only for the 2009-2010 season since other seasons have either no or insufficient data. Confidence intervals in these results are affected by actual variations in levoglucosan levels and shares as well as variations due to analytical reproducibility.

Table 1: Average levoglucosan (LG) levels and shares for four sites over the three year study period.

	State Building		Peger Road		North Pole		RAMS	
	LG Level (ng/m^3)	LG Share (%)	LG Level (ng/m^3)	LG Share (%)	LG Level (ng/m^3)	LG Share (%)	LG Level (ng/m^3)	LG Share (%)
2008-09	573 ±203	3.1 ±1.1	628 ±120	2.18 ±0.24	833 ±480	3.8 ±1.2	NA	NA
2009-10	671 ±288	2.33 ±0.63	312 ±131	1.60 ±0.41	1720 ±470	4.80 ±0.51	NA	NA
2010-11	671 ±157	2.96 ±0.32	763 ±195	2.30 ±0.36	1150 ±490	4.85 ±0.53	2680 ±1160	4.67 ±0.70
3 yr	632 ±118	2.80 ±0.46	628 ±120	2.18 ±0.24	1400 ±300	4.59 ±0.40		

Levoglucosan levels range from 600 to 2700 ng/m^3 with levels at the State Building and Peger Road at the lower end and those at North Pole averaging 1400 ng/m^3.

Table 2: Levoglucosan shares for various devices, fuels and burn rates.

Filter ID	Burner Type	Fuel Type	Burn Rate	Levoglucosan Share (%)
FNB 1	pellet	Pellet	single	0.24
FNB 44	conv. WS	Birch	high	1.08
FNB 40	conv. WS	Spruce	high	0.88
FNB 52	conv. WS	Birch	low	1.18
FNB 48	conv. WS	Spruce	low	0.35
FNB 4	Cert. WS	Birch	high	0.27
FNB 7	Cert. WS	Spruce	high	1.80
FNB14	Cert. WS	Birch	low	6.12
FNB 18	Cert. WS	Spruce	low	6.05
FNB 87	NQ OWHH	Spruce	high	5.86
FNB 27	EPA OWHH	Birch	high	7.46
FNB 34	EPA OWHH	Spruce	high	2.48
FNB 28	EPA OWHH	Birch	low	5.73
FNB 36	EPA OWHH	Spruce	low	11.73

The RAMS site, with an average of 2700 ng/m^3 is very high, but the PM$_{2.5}$ levels are also very high at that site. Levoglucosan share range from 1.6 to 4.7%, with the State Building and Peger Road sites averaging 2.2-2.8% and the North Pole and RAMS sites averaging 4.6-4.7%. Significant differences in levoglucosan levels and shares are observed between sampling sites, with the North Pole and RAMS sites showing higher levels and shares and the State Building and Peger Road sites having lower levels and shares. There are no significant differences or trends in levoglucosan levels or shares for any given site as a function of heating season. Variability in the levoglucosan levels, expressed as relative 95% confidence intervals, are high, often exceeding 40%. This variation reflects the fact that levoglucosan levels increase and diminish with $PM_{2.5}$ levels, which also vary significantly. Relative variations in levoglucosan as share of $PM_{2.5}$ are lower, and are typically 15% or less.

Fourteen filters generated by OMNI Scientific utilizing wood burning devices and two wood species representative of those from Fairbanks, and generated at different burn rates, were also analyzed for levoglucosan content and share. The results for levoglucosan share of the wood smoke $PM_{2.5}$ for these filters are presented in Table 2. Based on replicate analyses of some filters, the relative uncertainty in these numbers is estimated to be ±10%.

In general, these results indicate a relatively low share of levoglucosan in the wood smoke (3.7%) compared to published values[1-3]. No significant differences were observed in levoglucosan share based on wood species, which is also not consistent with previous studies[1-3]. Significant differences are observed as a function of burner type and within burner types as a function of burn rate.

2.3 Interpretation and Discussion

The levoglucosan results in Tables 1 and 2 have been analyzed in an effort to provide a quantitative measure of the contribution of residential wood combustion to ambient $PM_{2.5}$. Recent studies have made similar efforts[1]. The basic approach is to establish an experimental levoglucosan share in wood smoke, and to use this to convert levoglucosan share of ambient $PM_{2.5}$ to wood smoke fraction of ambient $PM_{2.5}$. Dividing the levoglucosan share of ambient $PM_{2.5}$ by the levoglucosan share of pure wood smoke generated using representative heating appliances and wood species should provide the fractional wood smoke contribution to the ambient PM. The levoglucosan share of wood smoke is established by analysis of PM from wood heaters and wood species used in the region of study. The levoglucosan share is generally observed to vary between wood species[1-3], so a representative value for the region is calculated as a weighted average based on a survey of the amount or fraction of each wood species consumed in the region[1].

There are several difficulties, however, in establishing the best conversion factor to apply to Fairbanks ambient levoglucosan results. The most relevant data for levoglucosan share of wood smoke $PM_{2.5}$ should be those reported in Table 2. However, those data include results only for spruce and birch, and a survey of wood consumption in Fairbanks has indicated 43% aspen, 52% birch, and 6% spruce. Further, average levoglucosan share reported in Table 2 is 3.7%, which is significantly lower than typical and average levoglucosan shares measured in ambient $PM_{2.5}$ at the North Pole and RAMS sites. Calculation of wood smoke contribution to ambient PM using these average numbers would result in average values of 124-126% for these two sites. This is clearly not a reasonable result.

There are experimental levoglucosan shares of PM reported in the literature for wood smoke from various species, including aspen, birch and spruce (Fine). These published data are generally accepted and have been used in multiple studies to interpret ambient PM levoglucosan results. The published numbers are generally higher than those reported in Tables 1 and 2, and employing them would result in more acceptable average wood smoke contributions of less than 100%. However, the published results are not specific for appliances and practices in Fairbanks, and their use thus introduces significant uncertainty. Other published results for levoglucosan share do not include the same species as those burned in Fairbanks and/or are for PM_{10} rather than $PM_{2.5}$.

We have investigated multiple approaches to generate a conversion factor to allow the calculation of wood smoke contributions from levoglucosan fractions of ambient $PM_{2.5}$. Each of our conversion factors is a weighted average based on the survey data for wood species consumption in Fairbanks:

$$CF = \frac{1}{0.43L_A + 0.52L_B + 0.06L_S}$$

where CF is the desired conversion factor and L_A, L_B, and L_S are the levoglucosan share for aspen, birch and spruce wood smoke respectively. A value calculated from results published by Caseiro et al. (CF=11) was rejected because those published results did not include all of the species of interest and because they were for PM_{10}. The value calculated from the published results of Fine et al. (CF=9.01) is considered the industry standard, and is based only on the assumption that the Fine results are valid for Fairbanks devices and conditions. This "Fine conversion factor" was the lowest of the calculated conversion factors and is used here as a lower limit. Two conversion factor values were calculated using, in part, the results in Table 2 for the OMNI-generated filters. The first is calculated using the average values for L_B and L_S from Table 2 under all burn conditions and the value for aspen reported by Fine et al. (L_A=0.125). The resulting "OMNI conversion factor" (CF=13.3) is strongly influenced (43%) by the published value for aspen. Working with a lower value for aspen more in line with those measured for OMNI-generated filters would result in a larger conversion factor and in many days for which wood smoke contributions in North Pole would exceed 100%. The OMNI conversion factor as calculated results in only one day for which wood smoke contribution in North Pole exceeds 100%, and three days that exceed 90%. It is thus a reasonable upper limit for the conversion factor. Finally, device type data by zip code was utilized together with wood species survey data to generate site-specific conversion factors weighted for both wood species and device type. These conversion factors were calculated using L_A from Fine et al., and L_B and L_S from Table 2 and ranged from 12.2-12.4. There was significant concern that these conversion factors were based on too many data with significant uncertainties. Because of this, and because the values are intermediate, they were rejected and were not used for additional calculations.

Using the two conversion factors it is possible to calculate a low and a high estimate of wood smoke contribution to ambient $PM_{2.5}$ in Fairbanks. The high end estimates are nearly 48% higher than the low end estimates. Table 3 presents these results by site and season, along with results for the same sites and seasons from ^{14}C and CMB analysis. The levoglucosan results include analyses for many sampling periods when ^{14}C analysis was not performed. Average values are reported, but these do not differ significantly from median values. Errors are reported as presented in previous reports or as 95% confidence intervals for levoglucosan results. The results for ^{14}C analysis are based on a subset of the samples that were analyzed for levoglucosan, and those results may thus be biased if those samples were not selected at random. Still, results calculated using the OMNI conversion factor (which includes the published Fine result for Aspen) are within the range or are not significantly different from the results reported from the ^{14}C results. Results calculated using the conversion factor generated using only the published Fine numbers are generally lower than, and often significantly lower than, the minimum value reported from the ^{14}C results. All of the results based on levoglucosan analysis are significantly lower than those reported using CMB modeling. It should be noted that some data were eliminated for a few low PM days, where the results for levoglucosan are either below the detection limit or near the detection limit and thus have considerable error. No more than two data points were eliminated for any heating season.

Table 3: Wood smoke contributions to ambient PM$_{2.5}$ as determined by ^{14}C analysis, levoglucosan analysis

	WS % PM$_{2.5}$ ^{14}C Minimum	**WS % PM$_{2.5}$ ^{14}C Maximum**	**WS % PM$_{2.5}$ Levoglucosan (Fine CF=9.01)**	**WS % PM$_{2.5}$ Levoglucosan (OMNI CF=13.3)**	**WS % PM$_{2.5}$ CMB Model (OMNI)**	**WS % PM$_{2.5}$ CMB Model**
State Bldng						
2008/2009	31.6 ± 8.0	38.0 ± 9.6	28.1±10.0	34.7±5.9	56.0	66.3 ± 10.1
2009/2010	36.7 ± 7.5	44.2 ± 9.1	21.0±5.6	31.0±8.3		69.9 ± 7.8
2010/2011	28.7 ± 4.3	34.5 ± 5.1	26.7±2.9	39.4±4.3		72.0 ± 6.3
3-yr avg	33.6 ± 7.7	40.4 ± 9.3	25.6±4.1	35.2±3.5		68.5 ± 8.6
North Pole						
2008/2009	42.9 ± 9.8	51.7 ± 11.8	36.8±10.0	54.3±14.7	73.4	72.1 ± 4.7
2009/2010	56.7± 6.3	68.3 ± 7.6	43.3±4.6	63.8±6.8		83.3 ± 10.3
2010/2011	58.4 ± 6.9	70.4 ± 8.3	43.7±4.8	64.3±7.0		73.8 ± 17.0
3-yr avg	55.0 ± 8.3	66.2 ± 10.0	42.0±3.4	61.8±5.1		79.4 ± 11.8
Peger Road						
2008/2009	23.6	28.4	14.3±3.7	21.1±5.4	51.0	62.9
2009/2010	33.9 ± 4.8	40.9 ± 5.8	21.5±2.9	31.7±4.3		69.9 ± 13.1
2010/2011	28.7 ± 6.6	34.6 ± 8.0	22.5±3.4	33.1±5.0		68.5 ± 11.3
3-yr avg	31.8 ± 5.6	38.3 ± 6.7	20.0±2.0	29.5±3.0		69.0 ± 12.1

The relatively low per sample cost of levoglucosan analysis allows multiple analyses to be run a single site in a single season and over several seasons. This, in turn, provides a means to monitor wood smoke contributions as a function of time as well as during and after efforts to reduce wood smoke emissions. A major caveat with this approach, however, is that source profiles would also need to be monitored if significant changes in fuels or devices are implemented. As an example of the approach, the wood smoke contribution to PM$_{2.5}$ at two sampling sites in Fairbanks as a function of time are presented in Figure 1. These plots show clearly that there is significant variability in the results, which is a combination of actual variability and random error in the measurements (if relative error in PM and levoglucosan measurements are each ±10%, the calculated levoglucosan share can be expected to be ±14%). The plots show no observable trend within any heating season. The data show a weak but statistically insignificant trend of increasing contribution from wood smoke over time. Neither these plots nor the average seasonal data in Table 3 provide significant evidence of any trend of increased or diminished wood smoke contribution over this time period.

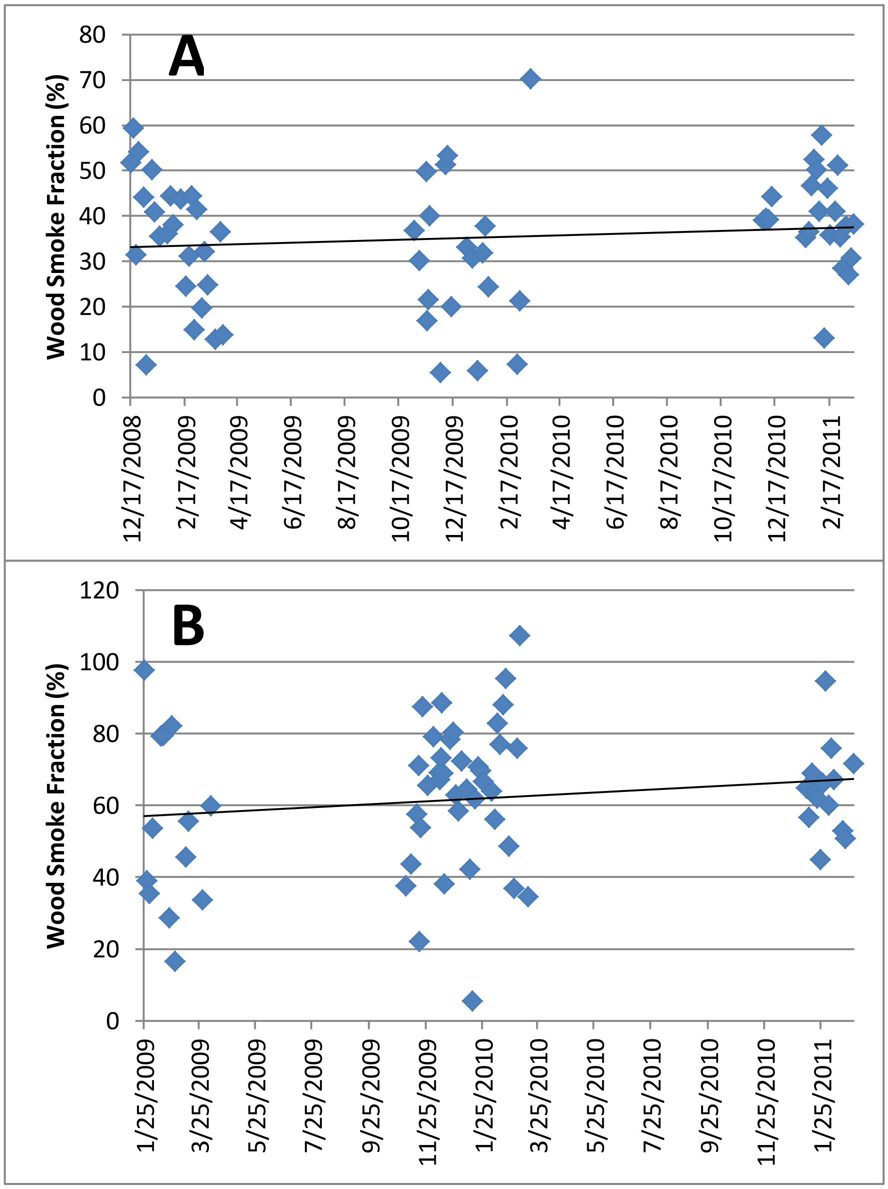

Figure 1: Wood smoke contribution to ambient $PM_{2.5}$ in Fairbanks North Star Borough, based on levoglucosan measurements and the OMNI conversion factor, at A. State Building and B. North Pole sites as a function of time.

2.4 Conclusions

Measurement of levoglucosan shares in ambient $PM_{2.5}$ in Fairbanks as well as in wood smoke particulate using representative devices and fuels allows an estimate of the residential wood smoke contribution to ambient $PM_{2.5}$. The final estimates include significant uncertainty due to both random measurement errors and lack of knowledge concerning the chemical composition of wood smoke. The effect of random measurement errors is reduced somewhat by the large number of measurements that can be made to generate averages. The effect of errors in estimation of the conversion factor is not diminished by making multiple measurements. Two conversion factors were generated that can be reasonably expected to yield minimum and maximum wood smoke contributions, but as an indication of the uncertainty these two values differ by nearly 45%.

The resulting values for wood smoke contribution are similar to those determined from ^{14}C analysis. This lends some level of credence to both of these methods. Both of the approaches, however, yield results that are significantly lower than those obtained from CMB analysis.

Levoglucosan analysis is relatively inexpensive in comparison to either ^{14}C analysis or CMB analysis. This allows the wood smoke fraction of $PM_{2.5}$ to be determined and monitored many times over the course of a heating season or intervention program. Inspection of the data for the past three years in the Fairbanks area indicates that wood smoke contribution has not diminished but may have increased.

3. Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAH) are found in the $PM_{2.5}$ from most combustion processes. Although the PAH are generally associated with combustion, certain PAH are reported to be strongly associated with combustion of specific fuels. Examples include retene, picene, and thiophenes, which are often associated with wood, coal and diesel fuel combustion, respectively.

Ambient and OMNI Scientific-generated $PM_{2.5}$ samples on quartz filters were submitted to the Desert Research Institute for analysis of PAH, including two thiophenes (dibenzothiophene and benzonaphthothiophene), on two dates. In the first round of analyses, eight ambient samples were analyzed for 62 PAH. In the second set, 25 ambient samples and 11 OMNI-generated samples were analyzed for 96 PAH. All of the ambient $PM_{2.5}$ samples are from the State Building site. The first eight samples were selected to be relatively high $PM_{2.5}$ days to ensure detection of the PAH, but the subsequent 25 ambient samples were selected considering meteorological conditions and represent a range of low to high $PM_{2.5}$ days. Most of the ambient samples are from the 2009-10 season. All of the raw and calculated results discussed in this report are provided in a spreadsheet.

The results for OMNI Scientific samples have been used to identify those PAH that appear at relatively high levels and shares of $PM_{2.5}$ in samples for specific fuels and devices. Those fuel-specific share data have then been used to set upper bounds on the contribution to ambient $PM_{2.5}$ from the combustion of those fuels.

3.1 OMNI Fuel and Device-Specific Samples

OMNI Scientific supplied UM with eleven quartz filter samples generated using various burners and fossil fuels. The identity of the filters, fuel and burner type are provided in Table 4. The $PM_{2.5}$ catch for each filter was calculated as described for OMNI-generated wood smoke filters as described in section 2.1. Unfortunately, no data were available to allow calculation of the $PM_{2.5}$ catch for two of the filters. Full PAH results for these filters, with analytical uncertainties, are provided in a spreadsheet.

Unfortunately, no replicate filters were provided for any fuel type or device, so it is not possible to estimate the repeatability of these experiments.

Table 4: OMNI Scientific-generated filters analyzed for PAHs.

Filter ID	**Fuel**	**Device**	**$PM_{2.5}$ Catch (µg)**
FNB56	No. 1 Fuel Oil	CHIF	NA
FNB59	No. 2 Fuel Oil	CHIF	474
FNB62	Waste Oil	Waste Oil Burner	9559
FNB66	Coal	Stove	NA
FNB69	Dry Coal	Stove	16340
FNB72	Dry Coal	Stove	2950
FNB79	Coal	Stove	7536
FNB89	Coal	OWHH	93786
FNB91	Coal	OWHH	59879
FNB95	Coal	HH Cold Start	3431
FNB96	Coal	HH Hot Start	3965

3.2 Fuel and Waste Oil

Insufficient data were provided by OMNI Scientific to calculate $PM_{2.5}$ catch for the filter generated with no. 1 fuel oil. The filter provided for no. 2 fuel oil has a relatively low catch of $PM_{2.5}$, and analysis was able to detect significant quantities and shares of only bibenzyl and 9-flourenone. Bibenzyl appears at a relatively high share of no. 2 fuel oil $PM_{2.5}$, at 0.2%. Although a higher quantity of $PM_{2.5}$ was caught for waste oil, analysis of this filter detected only 9-fluorenone and at a much lower share (0.0001%) compared with no. 2 fuel oil. The results for waste oil and no. 1 fuel oil do not identify any potential $PM_{2.5}$ markers for these fuels. It is possible, however, to consider 9-fluorenone and bibenzyl as markers of no. 2 fuel oil combustion.

9-Fluorenone made up a significant but small share (0.013%) of no. 2 fuel oil $PM_{2.5}$, but was also detected in the OMNI generated coal $PM_{2.5}$ samples at 0.0002% to 0.004% share. 9-Fluorenone was detected in ambient samples at similar to higher shares than in the no. 2 fuel oil $PM_{2.5}$ sample, implying that there is another significant source of this compound in ambient $PM_{2.5}$. This compound was thus not considered to be a unique or useful marker for no. 2 fuel oil $PM_{2.5}$.

Bibenzyl, however, was not detected in any other OMNI-generated fossil fuel $PM_{2.5}$ samples but was detected as a significant share (0.2%) in no. 2 fuel oil $PM_{2.5}$. Bibenzyl was not determined in the first set of eight ambient filter samples but was detected in 24 of the 25 samples submitted in the second set. Bibenzyl is found at much lower shares in ambient $PM_{2.5}$ than in $PM_{2.5}$ for no. 2 fuel oil. Bibenzyl was thus considered a potentially unique and useful marker for no. 2 fuel oil combustion.

An upper boundary for the contribution of no. 2 fuel oil $PM_{2.5}$ to the ambient $PM_{2.5}$ samples was calculated using the bibenzyl results for ambient shares and the experimental bibenzyl share in no. 2 fuel oil $PM_{2.5}$. **This analysis provided a median of 0.6% and a mean of 0.6 ± 0.4% (±1σ) contribution, suggesting that no. 2 fuel oil combustion is responsible for only a minor fraction of ambient $PM_{2.5}$.**

This is considered an upper boundary since the analysis does not take into consideration any other potential sources of bibenzyl. Further, there is significant but unquantifiable uncertainty in this result, since it is based on a single collection and analysis of $PM_{2.5}$ from no. 2 fuel oil.

3.3 Coal

OMNI Scientific provided $PM_{2.5}$ samples for coal combustion in various residential devices. These results provide some useful results for these devices. However, there are still no measured values for any PAH in coal emissions from power plants or other commercial facilities.

Inspection and analysis of the results for the OMNI coal $PM_{2.5}$ samples suggests eight possible PAH markers for coal combustion. These compounds were selected because they were detected in more than half of the OMNI coal $PM_{2.5}$ samples and because they showed at least a 200 ppm share for one or more coal $PM_{2.5}$samples. Table 5 lists the selected PAH with their median and average ± 1σ shares of $PM_{2.5}$ over the seven usable OMNI coal $PM_{2.5}$ samples. The very high standard deviations in these data reflect the large variability between different coal burning devices tested by OMNI scientific. In each case, $PM_{2.5}$ from the HH systems had the lowest shares of PAH compounds. Previous studies have identified picene as a unique marker for coal combustion,[4-6] and this compound is observed at relatively high shares in most of the coal $PM_{2.5}$ samples in this study (although not for the HH systems).

Table 5: PAH compound shares of coal $PM_{2.5}$ in OMNI Scientific-generated samples, and contributions of coal $PM_{2.5}$ to Fairbanks ambient $PM_{2.5}$ calculated using these shares.

Compound	**Share of Coal $PM_{2.5}$ (ppm)**		**Median Coal Fraction of Ambient $PM_{2.5}$ (%)**	
	Median	**Mean ± 1σ**	**by Median**	**by Mean**
Picene	1000	1000 ± 1200	2.7	2.7
Retene	56	250 ± 400	72	16
Indeno[1,2,3]pyrene	320	370 ± 350	19	16
Benzo[g,h,i]perylene	440	460 ± 430	26	24
Anthanthrene	210	190 ± 160	12	13
Dibenzo[a,l]pyrene	150	130 ± 120	4.4	4.9
Coronene	160	160 ± 150	21	21
Dibenzo(b,k)fluoranthene	160	160 ± 150	5.7	5.8
Dibenzothiophene	2.2	11 ± 14	234[1]	48[1]
Benzonaphthothiophene	6.4	19 ± 33	20[1]	6.7[1]

[1] Based on second set of 25 ambient $PM_{2.5}$ samples only.

Also included in Table 5 are the median percent contributions of coal $PM_{2.5}$ for the Fairbanks ambient $PM_{2.5}$ samples based on either the median or the mean share of that compound in OMNI-generated coal $PM_{2.5}$ samples. Most of these are determined for the full set of 33 ambient samples, but thiophene results are reported for only the latter 25 samples analyzed (this is discussed in detail below).

The results for coal $PM_{2.5}$ fraction based on the PAHs are highly variable, ranging from a median contribution of 2.7% to 72%. In fact, because these compounds are also produced by other combustion processes, each of the reported values is an upper boundary for coal $PM_{2.5}$ contribution. Retene, for example, is known to be emitted during wood combustion. Thus, the lowest of these calculated contributions, 2.7%, which is based on picene shares, is most likely to be valid. Picene has been reported as unique to coal combustion emissions[7,8], lending additional confidence to this result.

Defining a coal PM fraction based on any of the markers is complicated, however, by the wide range of $PM_{2.5}$ shares observed for each marker with different coal burning devices. Picene is no exception; picene shares range from below the detection limit (5 ppm share of $PM_{2.5}$) for HH systems to 3300 ppm share of $PM_{2.5}$ for coal stoves. This suggests that the median coal $PM_{2.5}$ contribution to ambient $PM_{2.5}$ could range from 0.8% if the contribution were exclusively from coal stoves to >100% if the $PM_{2.5}$ were exclusively from HH systems. A value of greater than 100% indicates a substantial contribution from a separate source, although other sources of picene have not been reported. It is possible that a single coal stove in the vicinity of the sampling site contributing less than 1% to the sampled $PM_{2.5}$ could account for all of the observed picene.

3.4 Ratiometric Analysis

Another commonly used measure for sourcing PAH emissions is the ratio of indeno[123-cd]pyrene to the sum of indeno[123-cd]pyrene and benzo[ghi]perylene (IP/(IP+BghiP)).[6,9,10] Typical values for this ratio from various fossil fuel sources, woodsmoke, and for Fairbanks are reported in Table 6. No published value is available for residential oil combustion $PM_{2.5}$. The ratio for OMNI-generated coal $PM_{2.5}$ (average ± 1σ) is also included in Table 6. No value could be determined for oil burner samples since these PAH compounds were not detected. The ratio for Fairbanks ambient $PM_{2.5}$ is reasonably consistent between samples, and is most similar to that reported for diesel fuel emissions. The observed ratio is lower than all reported ratios except gasoline autos, which suggests a significant contribution from transportation.

Table 6: Ratio of indeno[123-cd]pyrene to sum of indeno[123-cd]pyrene and benzo[ghi]perylene for various sources.

Source	IP/(IP+BghiP)
Gasoline autos	0.18
Diesel autos	0.37
Coal combustion	0.56
Wood combustion[9]	0.54
OMNI-Coal	0.42 ± 0.05
Fairbanks $PM_{2.5}$	0.33 ± 0.05

3.5 Thiophenes

The thiophenes are unique sulfur-containing compounds related to the PAHs that have been reported in the emissions of fossil fuel combustion. Preliminary studies of Fairbanks ambient $PM_{2.5}$ showed high levels of these compounds. Thus, there was interest in further study of these compounds in ambient $PM_{2.5}$ and in $PM_{2.5}$ from fossil fuel sources.

Dibenzothiophene, benzonapthothiophenes and alkylated derivatives of these compounds are reported to be representative of diesel fuel vehicle emissions.[7,8] These compounds make up a significant fraction of the sulfur content of diesel fuel. Low sulfur diesel fuel has lower concentrations, and vehicles utilizing low sulfur diesel fuel emit reduced quantities of these compounds[7,8]. Rogge *et al.*[11] did not report thiophenes in the emissions from residential fuel oil combustion, but Huffman *et al.* did report that typically 25-35% of the sulfur in residential fuel oil particulate is thiophenic sulfur.[12] Analysis of no. 2 fuel oil from Fairbanks at the University of Montana detected dibenzothiophene at 443 ppm, a level that is higher than that reported previously for high sulfur diesel fuel. Given the similar composition of # 2 fuel oil and diesel fuel, and the fact that the sulfur content of # 2 fuel oil is not regulated with respect to sulfur content, it was hypothesized by us that these compounds would be found in the $PM_{2.5}$ emissions from #2 fuel oil. Dibenzothiophene has also been reported in the emissions from gasoline vehicles[13]. In this and one report on diesel emissions[8], dibenzothiophene was found primarily in the gas phase. Given the ambient temperatures in Fairbanks, it seems likely that the compound would be found in the particulate phase. These sulfur compounds are not present in wood smoke $PM_{2.5}$.

Preliminary results for eight Fairbanks ambient $PM_{2.5}$ samples showed very high levels and shares of thiophenes when compared with published results for diesel emissions[7] or with ambient concentrations in European urban environments[14]. Results for the second set of 25 Fairbanks ambient $PM_{2.5}$ samples are much lower, however, and there is a large, statistically significant ($p<10^{-9}$), and inexplicable difference in thiophene shares of ambient $PM_{2.5}$ between the first eight and latter 25 samples. The share results for the latter 25 samples are lower than those reported for diesel emissions[7]. However, the ambient concentration results for the latter samples remain a factor of two to three higher than those reported for European cities[14]. This may be explained by different $PM_{2.5}$ concentrations and local environments. There is concern, therefore, that the thiophene results for the initial eight samples are invalid.

It is important to note that thiophenes were not detected in the OMNI-generated $PM_{2.5}$ from fuel oil samples. Our hypothesis that dibenzothiophene and benzonaphthothiopene might serve as markers for $PM_{2.5}$ from no. 2 fuel oil combustion is not supported by the results, and is invalidated.

Results for two thiophenes in OMNI-generated coal $PM_{2.5}$ are included in Table 5 and are used in subsequent calculations of coal contributions to ambient $PM_{2.5}$. Coal contributions based on thiophenes range from 6.7% to more than 100%. A value of greater than 100% indicates a substantial contribution from a separate source of dibenzothiophene, such as diesel or gasoline vehicle emissions.

It remains unclear what the sources of the thiophenes observed in Fairbanks ambient $PM_{2.5}$ are. None of the OMNI samples for residential oil heating devices had detectable levels of either thiophene, so this cannot be considered a significant source. Some fraction of the thiophene shares of Fairbanks ambient $PM_{2.5}$ may be explained by coal emissions, but these cannot explain all of the observed thiophenes. Previous studies have attributed thiophenes to diesel emissions, but this should be minimized with low sulfur diesel fuel. Previous studies have also reported relatively high concentrations of these thiophenes in the vapor phase emissions from gasoline automobiles[13]. It is possible in the winter climate in Fairbanks that these normally vapor phase emissions are associated with the $PM_{2.5}$, explaining a substantial fraction of the observed levels.

3.6 Conclusions

Polynuclear aromatic hydrocarbon and thiophene analysis of $PM_{2.5}$ generated using representative fuels and devices as well as ambient $PM_{2.5}$ does provide useful information regarding potential contributions of fuel oil, coal and potentially other fossil fuels to Fairbanks $PM_{2.5}$. The results indicate no substantial contributions of fuel oil or coal combustion to ambient $PM_{2.5}$.

No. 2 fuel oil emissions and waste oil filters had low amounts of $PM_{2.5}$ and the levels of nearly all compounds were below the detection limits. Bibenzyl was identified as a potential marker based on its relatively high fraction in no. 2 fuel oil $PM_{2.5}$ and its absence in coal $PM_{2.5}$. Using this as a marker leads to the conclusion that combustion of no. 2 fuel oil contributes a negligible fraction to ambient $PM_{2.5}$ of less than 1% for the 33 samples analyzed.

Picene is accepted as a unique marker for coal combustion. Zhang *et al.* reported picene as being "unique to the organic carbon emissions from coal combustion," although picene was not detected in all coal particulate and was notably absent from bituminous coal emissions from industrial boilers.[6] Zhang *et al.* did report picene in brown and mixed coal emissions from industrial boilers (3.7 and 2.0 ppm shares respectively) as well as much higher levels in the emissions from residential coal burners (72-284 ppm shares).[6] Oros *et al*. reported picene and methyl picenes as bituminous coal smoke markers, and C_2 substituted picenes as more general coal-specific markers.[4] As a large PAH, picene can be expected to be found primarily in the particulate phase.

The current results for picene support its use as a specific marker for coal combustion. Picene appears as a relatively large share of coal $PM_{2.5}$ for certain devices. Other compounds found in the coal $PM_{2.5}$ were detected at lower $PM_{2.5}$ share and suggested higher contributions of coal combustion to ambient $PM_{2.5}$. These compounds are very likely found in the emissions of other combustion sources.

Using a median value of picene share in the various devices leads to 2.7% coal contribution to $PM_{2.5}$. The picene shares, however, are highly variable depending on the device. If coal combustion were primarily from devices that have a much lower $PM_{2.5}$ share of picene, then coal $PM_{2.5}$ would represent a much higher fraction of ambient $PM_{2.5}$. Alternatively, the observed picene share of ambient $PM_{2.5}$ could result from less than a 1% contribution from devices that generate high picene shares.

The OMNI Scientific $PM_{2.5}$ samples do not show detectable levels of thiophenes for fuel oil samples, and show only low shares for coal samples. Thiophenes are observed in ambient $PM_{2.5}$ at levels that cannot be explained using coal combustion sources alone. It remains unclear what the sources or these thiophenes are. A fraction of the observed thiophenes might be associated with coal emissions, but it seems likely that the majority is from transportation sources.

4. Hopanes and Steranes

The hopanes and steranes are typically found and reported in distillate fossil fuel emissions, but have also been reported in coal emissions. The highest levels reported are for diesel auto emissions, and the lowest are for coal emissions. The hopanes and steranes are not present in emissions from biomass combustion, and thus provide a general indication of the extent to which an air shed is affected by fossil fuel emissions. Unfortunately, however, none of the compounds have been reported to be a specific marker of any particular fossil fuel source.

Analytical results for 23 hopane and sterane compounds have been obtained for eight Fairbanks ambient $PM_{2.5}$ samples, and generally show high levels and shares (5-60 ppm) of certain compounds. These results, with analytical uncertainties, are presented in a separate spreadsheet. Levels of hopanes and steranes in Fairbanks are typically higher than those reported for ambient air in other airsheds[5,15], and Fairbanks hopane and sterane shares are greater than those reported for most specific fuel emissions[4,6,8,11,13]. Analytical results for the same hopanes and steranes were also obtained for fossil fuel $PM_{2.5}$ samples provided by OMNI Scientific. These results are also presented in a separate spreadsheet.

4.1 Coal

Of the compounds analyzed, several hopanes were selected as potentially useful markers of coal combustion. Compounds were considered potential markers if they were detected in all of the coal $PM_{2.5}$ samples, if shares of three or more of the seven samples exceeded 100 ppm, and if the compounds did not have comparable shares in fuel oil $PM_{2.5}$. These selected hopanes, and their median and mean shares of coal $PM_{2.5}$, are presented in Table 7. Shares of coal $PM_{2.5}$ are highly variable between devices, with the HH systems showing low shares and the coal stoves generally showing high shares. In comparison, previous studies have reported hopane shares of diesel $PM_{2.5}$ of 5-60 ppm[7,8] .

Table 7: Hopane compound shares of coal $PM_{2.5}$ in OMNI Scientific-generated samples, and contributions of coal $PM_{2.5}$ to Fairbanks ambient $PM_{2.5}$ calculated using these shares.

Compound	**Share of Coal $PM_{2.5}$ (ppm)**		**Median Coal Fraction of Ambient $PM_{2.5}$ (%)**	
	Median	**Mean ± 1σ**	**by Median**	**by Mean**
17α(H),21ß(H)-29-Norhopane	83	122 ± 133	50	34
17α(H),21ß(H)-Hopane	111	126 ± 121	23	21
22S-17α(H),21ß(H)-30-Homohopane	45	132 ± 135	39	13
22R-17α(H),21ß(H)-30-Homohopane	90	137 ± 156	26	17
22S-17α(H),21ß(H)-30,31-Bishomohopane	41	65 ± 62	21	13

The share data presented in Table 7 can be used to estimate coal contributions to the ambient $PM_{2.5}$ samples. These results are also presented in Table 7, and show median coal contributions to ambient $PM_{2.5}$ of 13 to 50%. Because the hopanes are not specific to coal emissions, these should be considered upper bounds to coal contribution. Further, the hopane shares are highly variable with coal burning device. Thus, ambient levels of $PM_{2.5}$ could suggest an upper bound of as little as 6% contribution of $PM_{2.5}$ from coal stoves that produce high hopane shares. Coal emissions from HH systems, on the other hand, cannot explain the shares observed in Fairbanks ambient $PM_{2.5}$.

4.2 Fuel Oil

The results for hopane and sterane shares of no. 2 fuel oil and waste oil $PM_{2.5}$ were also examined for potentially useful selective markers. Hopane and sterane shares of waste oil $PM_{2.5}$ were all less than 1.3 ppm and were equivalent or higher in coal $PM_{2.5}$, and thus could not be used to estimate waste oil contributions to ambient $PM_{2.5}$. One sterane, 20S-5α(H),14ß(H),17ß(H)-cholestane, did appear at a relatively high share of no. 2 fuel oil $PM_{2.5}$ (13 ppm) and at lower shares of coal $PM_{2.5}$ (0-6 ppm). Using this compound as a marker for no. 2 fuel oil generates an extreme upper bound of 15% for the contribution of no. 2 fuel oil combustion to ambient $PM_{2.5}$. This is very clearly an overestimate to fuel oil contribution, since substantial quantities of this sterane would also be produced by combustion of other fossil fuels, including coal. Further, there is significant but unquantifiable uncertainty in this result, since it is based on a single collection and analysis of $PM_{2.5}$ from no. 2 fuel oil.

4.3 Ratiometric Analysis

An alternative approach for the analysis of hopane results is to calculate the ratio of 17α (H) 21β (H) hopane to 22R-17α (H), 21β (H) homohopane.[4,6,16] This value has been reported to be 3.7 for gasoline emissions and 2.5 for diesel emissions.[16] Unfortunately, conflicting results have been reported for coal combustion emissions, with Oros *et al.*[4] reporting values of 0.1-2.6 and Zhang *et al.*[6] reporting values of 4.28-9.19. In the current study, the ratio for OMNI-generated coal emissions over all devices ranged from 0.76 to 1.63 with a median of 1.15 and an average ± 1σ of 1.13 ± 0.33. The ratios for no. 2 fuel oil and waste oil emissions were found to be 0.57 and 1.01 respectively, but the ratio for no. 1 fuel oil emissions could not be determined because 22R-17α (H), 21β (H) homohopane was not detected. The average value observed for Fairbanks is 1.2 ± 0.4. This relatively low result for Fairbanks is not significantly different from that observed for the OMNI-generated coal filters and is within the range reported by Oros *et al.* for coal. This analysis implies that coal or other low ratio emissions such as fuel oil may be a more substantial contribution to the hopanes in Fairbanks ambient $PM_{2.5}$ than the analyses above suggest.

4.2 Conclusions

Hopane and sterane analysis of Fairbanks ambient $PM_{2.5}$ shows levels and shares that are indicative of substantial contribution from fossil fuel combustion sources. Unfortunately, however, none of these compounds can be considered specific markers of any individual combustion source. This means that any simple calculations of contributions from a given source will overestimate the value and must be considered upper bounds. Upper boundaries for the contributions of coal and no. 2 fuel oil combustion to ambient $PM_{2.5}$ by this approach are estimated to be 13% and 15% respectively.

Analysis based on the ratio of levels for two specific hopanes indicate that a substantial share of hopanes in ambient Fairbanks $PM_{2.5}$ are from a low ratio source such as fuel oil or coal. This is inconsistent with the results based on hopane and sterane shares of $PM_{2.5}$.

A more comprehensive approach of source apportionment using full profiles of all sources and ambient $PM_{2.5}$ is much more appropriate for this analysis. This is not recommended with the limited data available for Fairbanks sources and ambient $PM_{2.5}$.

5. References Cited

[1] Caseiro, A., Bauer, H., Schmidl, C., Pio, C. A., Puxbaum, H., "Wood burning impact on PM10 in three Austrian regions," *Atmospheric Environment* **2009**, *43*, 2186-2195.

[2] Fine, P. M., Cass, G. R., Simoneit, B. R. T., "Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Wood Types Grown in the Midwestern and Western United States," *Environmental Engineering Science* **2004**, *21*, 387-409.

[3] Schmidl, C., Marr, I. L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., "Chemical characterization of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions," *Atmospheric Environment* **2008**, *42*, 126-141.

[4] Oros, D. R., Simoneit, B. R. T., "Identification and emission rates of molecular tracers in coal smoke particulate matter," *Fuel* **2000**, *79*, 515-536.

[5] Rutter, A. P., Snyder, D. C., Schauer, J. J., De Minter, J., Shelton, B., "Sensitivity and Bias of Molecular Marker-Based Aerosol Source Apportionment Models to Small Contributions of Coal Combustion Soot," *Environmental Science and Technology* **2009**, *43*, 7770-7777.

[6] Zhang, Y., Schauer, J. J., Zhang, Y., Zeng, L., Wei, Y., Liu, Y., Shao, M., "Characteristics of Particulate Carbon Emissions from Real-World Chinese Coal Combustion," *Environmental Science and Technology* **2008**, *42*, 5068-5073.

[7] Liang, F., Lu, M., Birch, M. E., Keener, T. C., Liu, Z., "Determination of polycyclic aromatic sulfur heterocycles in diesel particulate matter and diesel fuel by gas chromatography with atomic emission detection," *Journal of Chromatography, A* **2006**, *1114*, 145-153.

[8] Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T., "Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks," *Environmental Science and Technology* **1999**, *33*, 1578-1587.

[9] Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T., "Measurement of Emissions from Air Pollution Sources. 3. C1-C29 Organic Compounds from Fireplace Combustion of Wood," *Environmental Science and Technology* **2001**, *35*, 1716-1728.

[10] Stracher, G. B., Taylor, T. P., "Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe," *International Journal of Coal Geology* **2004**, *59*, 7-17.

[11] Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., "Sources of Fine Organic Aerosol. 8. Boilers Burning No. 2 Distillate Fuel Oil," *Environmental Science and Technology* **1997**, *31*, 2731-2737.

[12] Huffman, G. P., Huggins, F. E., Shah, N., Huggins, R., Linak, W. P., Miller, C. A., Pugmire, R. J., Meuzelaar, H. L. C., Seehra, M. S., Manivannan, A., "Characterization of fine particulate matter produced by combustion of residual fuel oil," *Journal of the Air & Waste Management Association* **2000**, *50*, 1106-1114.

[13] Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T., "Measurement of Emissions from Air Pollution Sources. 5. C1-C32 Organic Compounds from Gasoline-Powered Motor Vehicles," *Environmental Science and Technology* **2002**, *36*, 1169-1180.

[14] Saarnio, K., Sillanpaa, M., Hillamo, R., Sandell, E., Pennanen, A. S., Salonen, R. O., "Polycyclic aromatic hydrocarbons in size-segregated particulate matter from six urban sites in Europe," *Atmospheric Environment* **2008**, *42*, 9087-9097.
[15] Zheng, M., Cass, G. R., Schauer, J. J., Edgerton, E. S., "Source Apportionment of PM2.5 in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers," *Environmental Science and Technology* **2002**, *36*, 2361-2371.
[16] Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., "Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks," *Environmental Science and Technology* **1993**, *27*, 636-651.