

Final report: Measurement of the contribution of biomass combustion to PM_{2.5}

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Background

This study aimed to develop innovative analyses in order to establish chemical markers to identify fine particulate pollution coming from wood burning. There are four distinct components to this project, under one overarching question:

“Can levoglucosan be used as a quantifiable tracer for predicting wood smoke contributions to PM_{2.5} mass in the Puget Sound area?”

The specific objectives of the project were as follows:

- An evaluation of a different analytical method for measuring levoglucosan used by other participating researchers.
- Conduct a laboratory intercomparison exercise involving two different analytical approaches for measuring levoglucoan on archived filter samples.
- Conduct a reassessment of a previously published source apportionment model for the Beacon Hill area of Seattle, focusing on the contribution of woodsmoke to ambient PM_{2.5} at this location.
- Evaluate the presence and spatial variability of Levoglucosan at selected PM_{2.5} monitoring stations in the Puget Sound area.

This study focused primarily on air pollution episodes and locations dominated by biomass smoke emissions from residential wood burning devices used for home heating. A simple air monitoring procedure is desired that would permit the quantification of the contribution of biomass smoke to ambient PM, in order to verify the extent to which biomass smoke contributed to the high PM events in these communities, and to guide the implementation of public health policies designed to reduce PM_{2.5} levels. Measurement of biomass smoke derived chemical markers, such as levoglucosan, shows promise as a tool for evaluating the contribution of biomass smoke to ambient fine PM_{2.5}. Results from this study will aid air quality managers in making informed decisions to target high wood smoke areas and implement wood smoke reduction initiatives, and potentially will guide future similar monitoring studies that use archived Teflon filters.

Results

Analytical method development and validation.

As requested by the USEPA's sponsor, OAQPS, we evaluated the feasibility of applying an aqueous extraction procedure to 47mm Teflon FRM filters, and coupling the aqueous extraction with our standard method for derivatization of the levoglucosan and GC/MS analysis. An extensive series of experiments were undertaken to try and couple aqueous

extraction methodology with derivatization and GC/MS analysis of the levoglucosan. Ultimately, we found that levoglucosan recoveries from spiked filters were unacceptably low (<60%) when using the aqueous extraction procedure (see Table 1). This appears to be due in part to the long drying time at elevated temperature required to remove water from the sample extract, in order to make the extract compatible with the derivatization chemistry used for the levoglucosan analysis. Therefore we elected to revert to our previously successful ethylacetate extraction procedure to permit accurate and sensitive quantification of levoglucosan. The lack of success with aqueous extraction, and the consequent need to use an alternate solvent (ethylacetate) for extraction, prevents us from being able to provide measurement of water soluble organic carbon, or water soluble potassium, for samples analyzed in this project.

Table 1: Comparison of levoglucosan recovered from spiked matrix using aqueous or organic extraction solvents.

	Aqueous extraction	Organic extraction
Average recovery (%)	24-57	72±9

It is important to note that the low recoveries we reported in Table 1 for the aqueous extraction procedure do not mean that aqueous extraction generally does not work for analysis of levoglucosan. What we found was specifically that the combination of aqueous extraction; drying of the extract, then derivatization and GCMS resulted in low recoveries for levoglucosan. In contrast, Collett and colleagues at Colorado State University do not use GC/MS analysis in their procedure for levoglucosan analysis - they combine aqueous extraction with HPLC-pulsed amperometric detection. Therefore they do not need to dry and derivatize their extracts as we have to do. Consequently they did not encounter the same recovery problems that we did when we attempted aqueous extraction.

On the other hand, the ethylacetate extraction procedure coupled with derivatization and GC/MS analysis using selected ion monitoring (SIM) proved to be robust, reproducible and sensitive (see table 2). The assay permitted us to reliably detect and quantify levoglucosan in single 24 hour partisol filters – even during the summer months when woodsmoke PM was low, and at locations that were not dominated by woodsmoke derived PM. This procedure has previously been published in detail (Simpson et al, 2004; Ward et al., 2006), and validated in a published interlaboratory method comparison study (Ward et al., 2006).

Table 2: Analytical figures of merit for determination of levoglucosan using the ethylacetate extraction procedure.

Number of samples analyzed	300
Average recovery (%)	72±9
Limit of detection (µg/filter)	0.05
Average concentration (µg/filter)	17.3
Range of concentrations measured (µg/filter)	0.08 - 239

An additional interlaboratory comparison exercise was conducted with another participating laboratory, in order to compare the performance of the two laboratories' extraction and analysis methods when applied to urban PM samples. PM was collected in Phoenix during June-August 2005 on quartz fiber filters using a high volume sampler. Stainless steel punches were used to remove duplicate 37mm diameter sections from nine of the filters, which were then extracted and analyzed at the University of Washington (UW), using the organic extraction procedure. Levoglucosan concentrations were measured in the filter sections, and compared with measurements obtained by the Collett laboratory at Colorado State University (CSU) using their aqueous extraction procedure and HPLC analysis with pulsed amperometric detection. These results are summarized in Table 3 and Figure 1.

Table 3: Levoglucosan measurements from Phoenix filters: method intercomparison study.

	UW measurements	CSU Measurements
Average Levoglucosan concentration ($\mu\text{g}/\text{m}^3$)	0.0015	0.020
Average Levoglucosan recovery*	$55 \pm 7\%$	NR
Agreement between duplicate measures (%)	$\pm 5\%$	NR

* based on recovery of d7-levoglucosan standard
NR= not reported

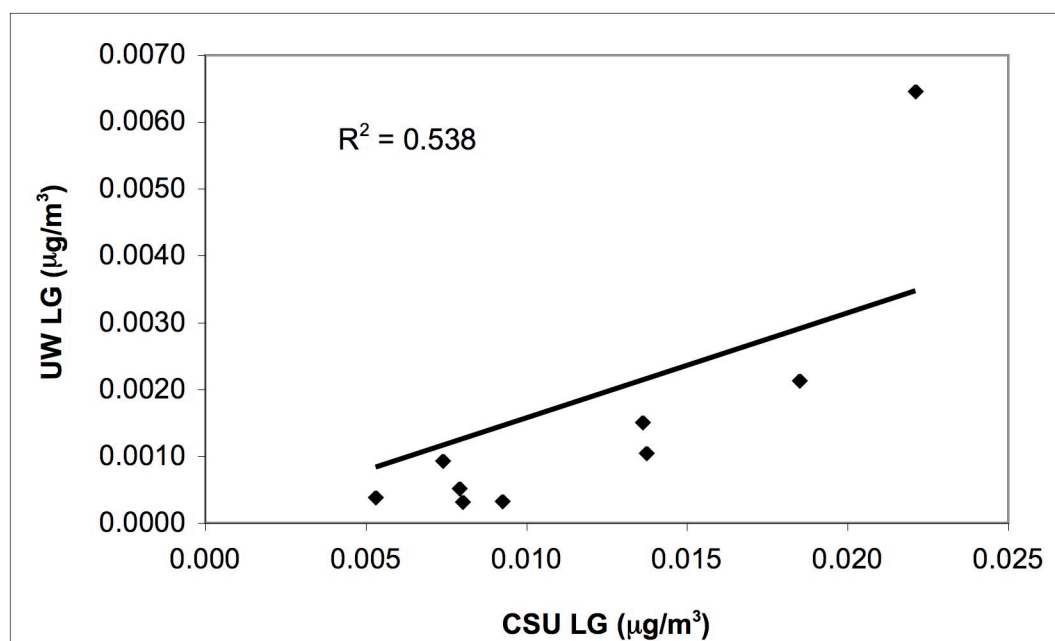


Figure 1: Scatter plot showing association between levoglucosan measurements from UW laboratory and CSU laboratory.

As shown in Table 3, the levoglucosan concentrations as determined by the UW laboratory were on average only about 15% of the values determined by the CSU laboratory. As shown in Figure 1, the concentrations from the two laboratories were

correlated with each other ($r^2 = 0.538$), although one filter with unusually high concentrations of levoglucosan appeared to be an outlier. If this sample is not included in the correlation, the r^2 value increased to 0.712, but the slope dropped to 0.092. At present there is no obvious explanation for the discrepancy between results obtained from the different laboratories. The within-laboratory QC measurements for the UW data are acceptable, with an average precision for duplicate extraction from the same filter of $\pm 5\%$ and an average recovery (based on recovery of the d7-levoglucosan spike in each sample) of $55 \pm 7\%$. Note that in comparison to levoglucosan measurements from the Teflon filters, recovery for these glass fiber filters was somewhat lower ($55 \pm 7\%$ versus $72 \pm 9\%$).

Based on the data in table 3, we cannot conclude why the values obtained differ between the two laboratories, or which (if any) of the two methods is inaccurate. However, in comparing the results from the CSU and UW laboratories, it is helpful to consider differences between the two methods. As noted previously the UW procedure involved organic extraction of a section of the quartz high-vol filters, followed by derivatization gas chromatographic separation of the analytes and mass spectrometric detection and quantification. In contrast, the CSU procedure utilized aqueous extraction, HPLC separation and amperometric detection. The comparison utilized sections from several quartz high-vol filters, whereas the organic extraction procedure was designed and validated using Teflon filters. Finally, unlike the partisol filters analyzed for subsequent sections of this report, the quartz high-vol filters were stored at ambient temperature and were not protected from sunlight. These latter factors could potentially contribute to degradation of levoglucosan on the archived filters over time.

A second intercomparison exercise is planned by the UW and CSU laboratories, using co-located, duplicate Teflon filters from a woodsmoke impacted location (Darrington WA; collected during January 2008), collected using a Partisol sampler. Results of the second intercomparison study will be included as an addendum to this report.

Measurement of woodsmoke contribution to $PM_{2.5}$ at Beacon Hill, Seattle WA.

A $PM_{2.5}$ source apportionment study was recently conducted for the Beacon Hill air monitoring site in Seattle (Maykut et al., 2003). The study concluded that vegetative burning (primarily residential wood combustion) contributed on average 29% of the ambient $PM_{2.5}$ at this location. The original study utilized the positive matrix factorization (PMF) procedure to generate the source apportionment model, based on measurements of $PM_{2.5}$ mass, trace metals, organic carbon (OC) and elemental carbon (EC). We decided to re-evaluate this source apportionment model, including additional measurements of levoglucosan as a woodsmoke source-specific tracer.

The atmospheric particle samples analyzed in this experiment were collected in the winter of 1996-1999 by the Puget Sound Clean Air Agency at the Beacon Hill sampling site. The Beacon Hill site is a representative urban residential area. It is located 100 m above sea level within a water reservoir site. Directly to the north and east, the area is residential. Large freeways are located to the north and west of the site. Additionally, the valley below the site includes warehousing facilities, a marine cargo port, and several other industrial sources including a brewery. In spite of some industrial impact, $PM_{2.5}$ samples from this site are likely to be impacted by both vehicular and

residential emissions and considered representative of exposures within a 20 km radius of the site (Goswami, 2002). $PM_{2.5}$ mass, trace metals, OC and EC have previously been determined in these samples, and a source apportionment analysis undertaken on these samples using positive matrix factorization (PMF) (Maykut et al., 2003). Subsequently, we have measured the concentration of the biomass-smoke specific tracer levoglucosan in a subset of 100 of the above samples collected at the Beacon Hill location.

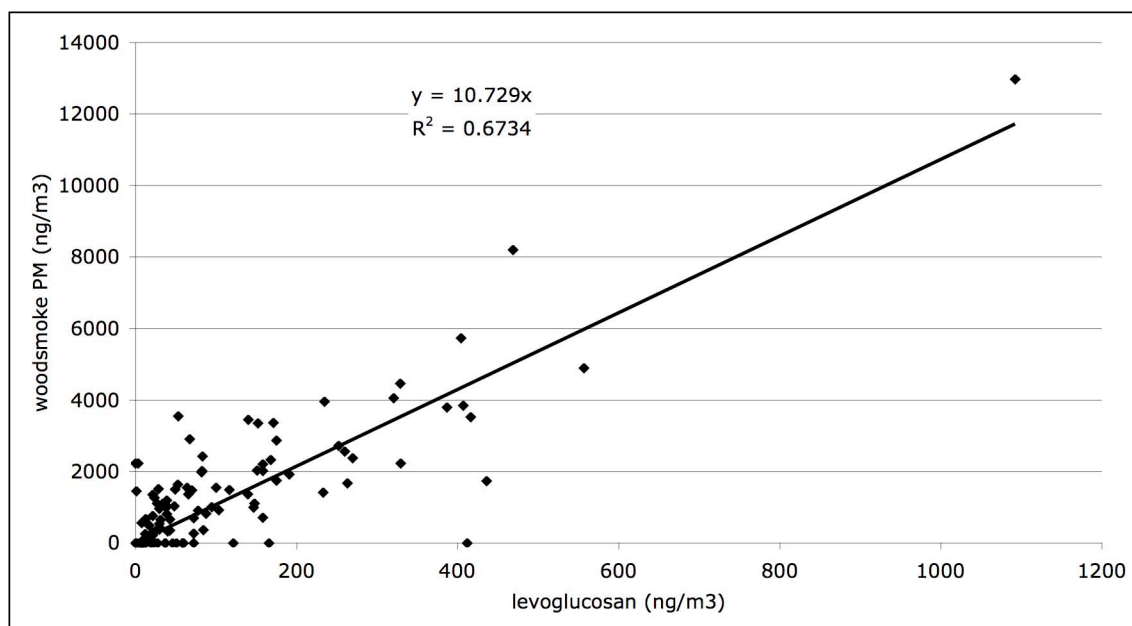


Figure 2: Association between measured levoglucosan concentrations and PMF-derived estimates of woodsmoke derived PM at the Beacon Hill air quality monitoring site in Seattle.

Figure 2 illustrates the association between the “woodburning factor” Maykut et al identified from their PMF analysis and levoglucosan measurements on the same filter samples. The correlation coefficient between the two variables is 0.83. From the slope of figure 2, we calculate that 9.3% of the estimated *woodsmoke derived* $PM_{2.5}$ mass is levoglucosan. This value is an estimate of the scaling factor that can be used to deduce ambient woodsmoke derived PM mass from measurements of levoglucosan on filter samples.

The use of a levoglucosan scaling factor is a simple way to estimate the contribution of woodsmoke to ambient $PM_{2.5}$ concentrations. In combination with other chemical speciation measurements the levoglucosan data may also be of use in receptor based models used to apportion ambient PM amongst various PM sources in an airshed.

The 100 samples from the Beacon Hill air quality monitoring site in Seattle were also examined in a PMF analysis, utilizing the PMF 1.1 software package. Two models were evaluated – one which included levoglucosan as an input variable, and one which did not include levoglucosan. The final results for the model including levoglucosan give a mean

value of 970 ng/m^3 (5 – 95% CI: 870-1050) of $\text{PM}_{2.5}$ that is attributable to the combustion of wood at this receptor site. The PMF 1.1 model includes bootstrapping calculations that enable determination of 5 – 95 % confidence intervals (as shown in Figure 3) for source contributions. By this calculation, an average of $12 \pm 1\%$ of the $\text{PM}_{2.5}$ at this site is due to the combustion of wood. The PMF-derived estimates of the woodsmoke source contribution in the present study differ substantially from results obtained previously for these samples by Maykut et al., (2003). Our analysis apportioned 12% of $\text{PM}_{2.5}$ to woodsmoke, whereas the corresponding estimates using the PMF model of Maykut et al. were 29% overall. The PMF model with levoglucosan identifies 6 distinct sources rather than 5, isolating the “vegetative burning” from the “mobile” and “Na-rich” sources (Figure 3). Thus the inclusion of levoglucosan as an input variable permitted resolution of the wood burning source, which was not possible without levoglucosan. However, it should be noted that in comparison with Maykut’s results, neither of our models completely resolved all of the major PM sources. We were limited by the available data to only including 100 samples in our PMF models, and we recognize that this comparatively small number of samples limits the robustness of our model.

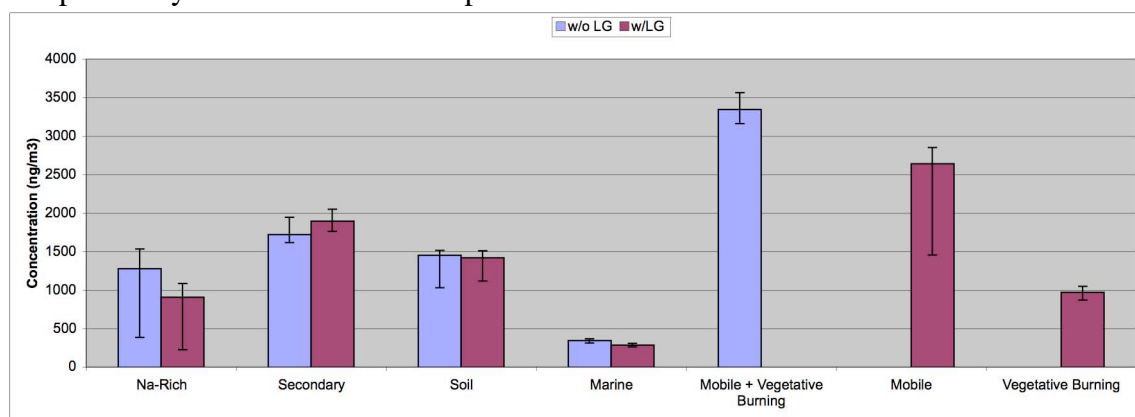


Figure 3: A comparison of the source contribution estimates as calculated by PMF with levoglucosan and PMF without levoglucosan. Error bars represent 5th and 95th percent confidence intervals.

Measurement of spatial variation in $\text{PM}_{2.5}$ and woodsmoke markers in the Puget Sound air shed.

In the final objective of this study we proposed to examine the spatial variation of $\text{PM}_{2.5}$ and woodsmoke markers in the Puget Sound air shed. The primary woodsmoke marker of interest was levoglucosan.

In order to examine the spatial variation of woodsmoke in the Puget Sound air shed, we developed a weighted-random sampling procedure to select 300 $\text{PM}_{2.5}$ filters from five locations in the Puget Sound air shed (Darrington, Tacoma_South, Marysville, Seattle_Beacon Hill and Seattle_Duwamish Valley). The filters were collected using Partisol samplers, by the Puget Sound Clean Air Agency (PSCAA) and the Washington State Department of Ecology. They were collected according to the appropriate FRM method, and the filters were archived in cold storage after filter weighing and prior to extraction and levoglucosan analysis. Locations of the air monitoring sites are illustrated

in the map shown in Figure 4. This map also illustrates the spatial distribution of residential woodstove use, based on data from the 2000 census. Filters were selected from the period March 2004 – February 2006, with the exception of the Darrington site, for which we selected filters from 2006-2007 because this site was not in operation prior to 2006. Sixty filters were selected from each of the 5 locations, including 40 filters per site from the heating season (October-February) and 20 filters per site from the non-heating season (March-September). The sampling date with the maximum particulate concentration from each site was preselected and all dates with particulate concentrations less than $3.0 \mu\text{g}/\text{m}^3$ were excluded. Sampling dates in which collection occurred at all four sites were pooled and then stratified into high, medium and low particulate concentration groups. Sampling dates were randomly selected from each group with even sampling frequency amongst the groups.

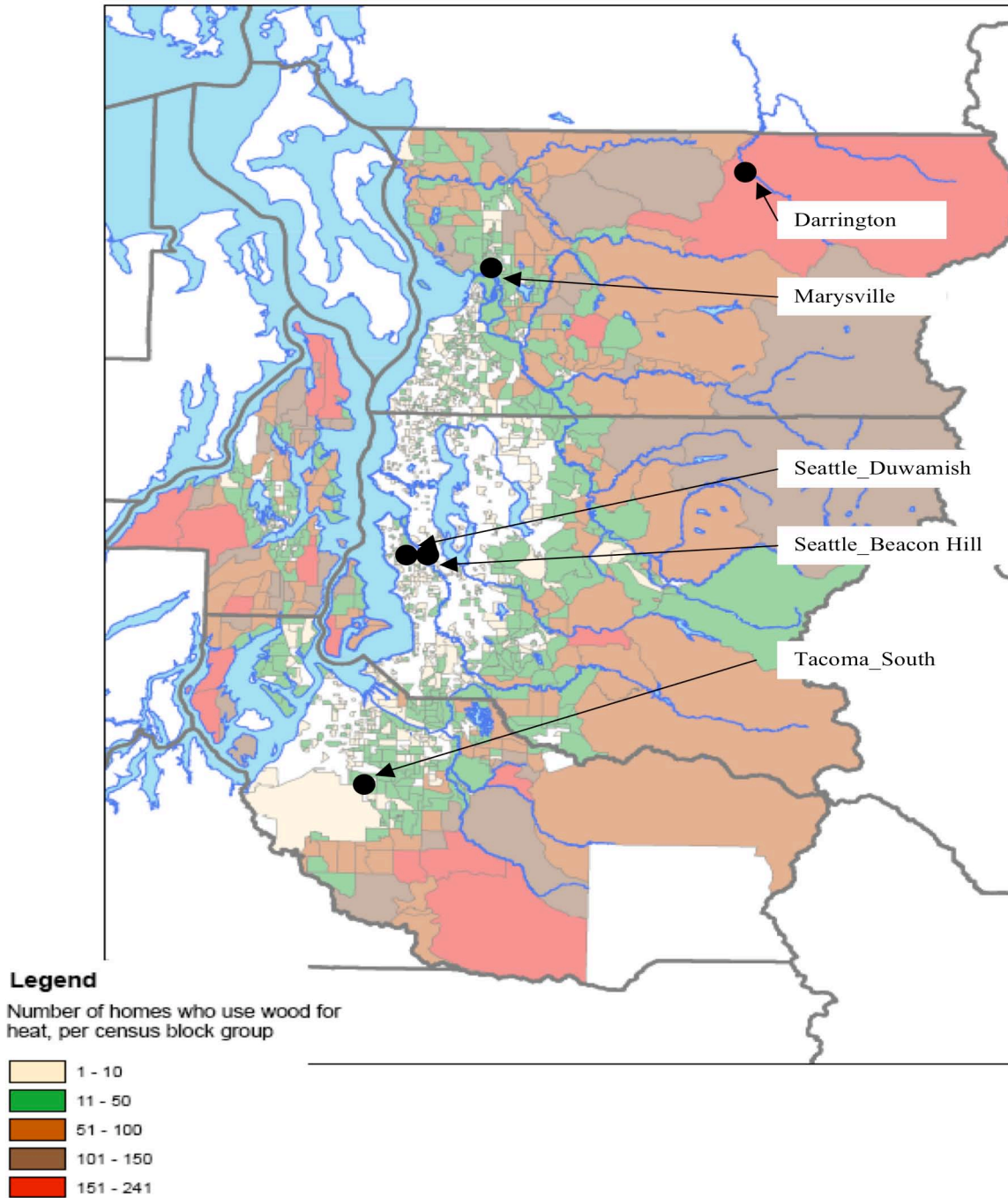


Figure 4: Map of Puget Sound Airshed indicating spatial distribution of residential woodstove use and locations of air monitoring sites.

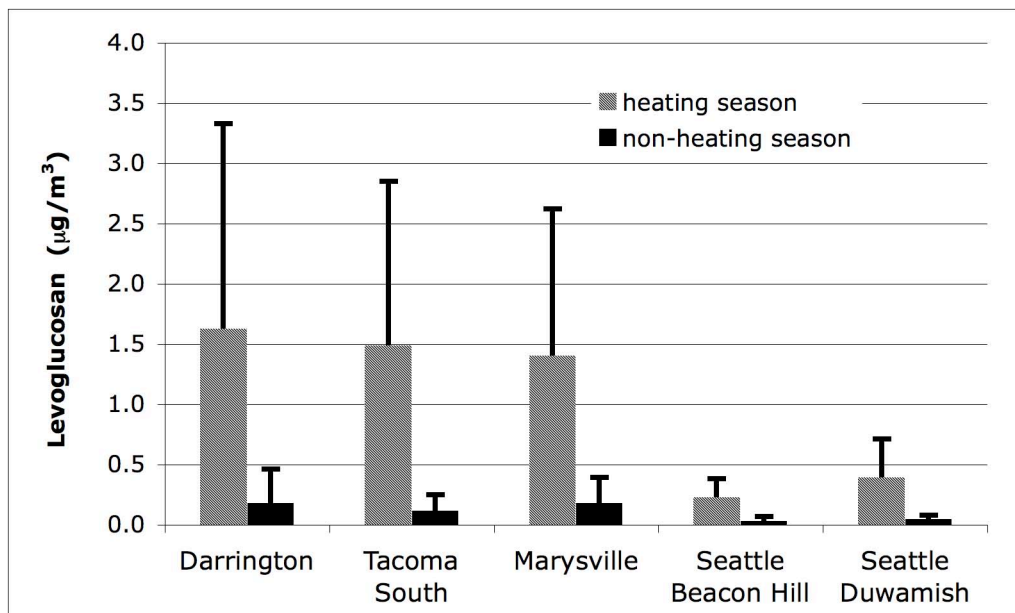


Figure 5: Spatial variation in levoglucosan concentrations in the Puget Sound airshed in heating and non-heating seasons. Error bars represent ± 1 SD.

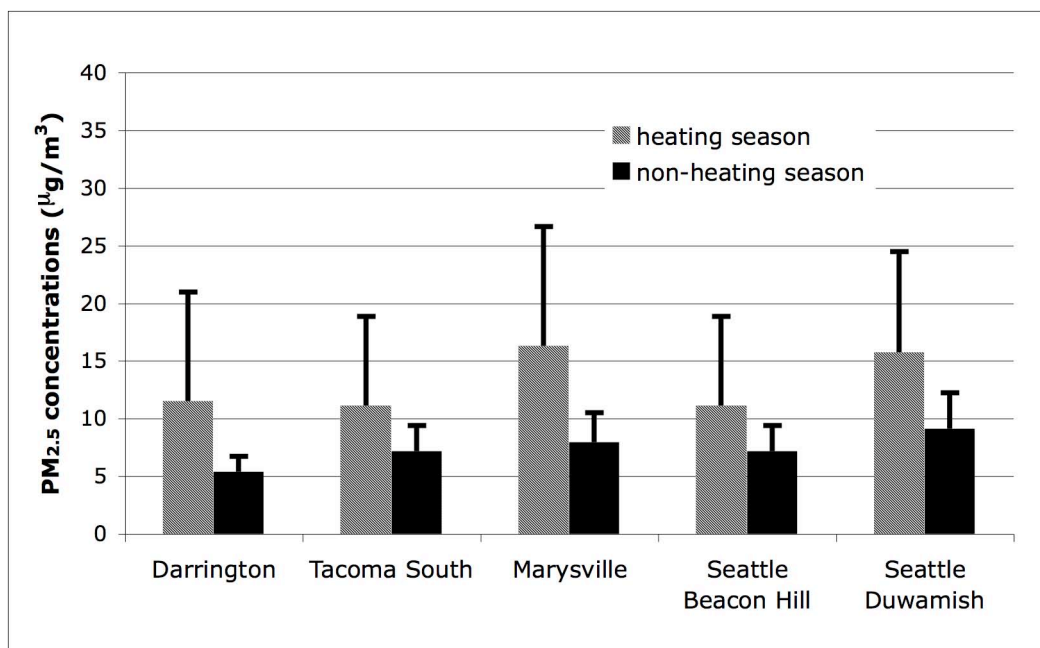


Figure 6: Spatial variation in PM_{2.5} concentrations in the Puget Sound airshed in heating and non-heating seasons. Error bars represent ± 1 SD.

Filters were analyzed for levoglucosan using the organic extraction procedure described earlier. These data are summarized in Figure 5. The associated PM_{2.5} concentrations are included in Figure 6. These data show that levoglucosan concentrations during the

heating season were relatively high at three locations (Darrington, Tacoma_South and Marysville), but the levoglucosan concentrations were 4-5 fold lower at the other two sites (Seattle_Beacon Hill and Seattle_Duwamish). At each site, levoglucosan concentrations were approximately 10-fold lower in the non-heating (summer season) compared to the heating season. In contrast to the levoglucosan data, little spatial variation in $PM_{2.5}$ concentrations was observed – average $PM_{2.5}$ concentrations were similar for all five monitoring sites. At all locations, $PM_{2.5}$ concentrations in the heating season were approximately two-fold higher than the $PM_{2.5}$ concentrations in the non heating season.

These observations are consistent with our *a priori* assumptions regarding the major contributions to fine PM. The three sites with high wintertime concentrations of levoglucosan: Darrington, Tacoma_South and Marysville, are all suburban or rural residential communities with a high prevalence of wood-burning devices used in residences for wintertime heating. The map in Figure 4 shows a high prevalence of residential woodstove use in the vicinity of these three sites. Two additional figures, showing the immediate vicinity of the Marysville and South Tacoma sites are included in the appendix to this report. These figures illustrate a high density of residential woodstove use in the immediate vicinity of the Marysville and South Tacoma sites. The Seattle_Beacon Hill location is the site of the regional EPA air monitoring site and is located southeast of the Seattle central business district. It is also close to the intersection of two major interstates freeways. The Seattle_Duwamish location is an urban site, south of the Seattle central business district and close to the Port of Seattle. It is also in close proximity to several major roadways, and is expected to be heavily impacted by diesel exhaust from the Port, from the roadways, and from industry in the immediate vicinity of the site. In contrast to the three high-woodsmoke sites, figure 4 indicates that there is little residential woodstove use in the vicinity of the two Seattle-area sites.

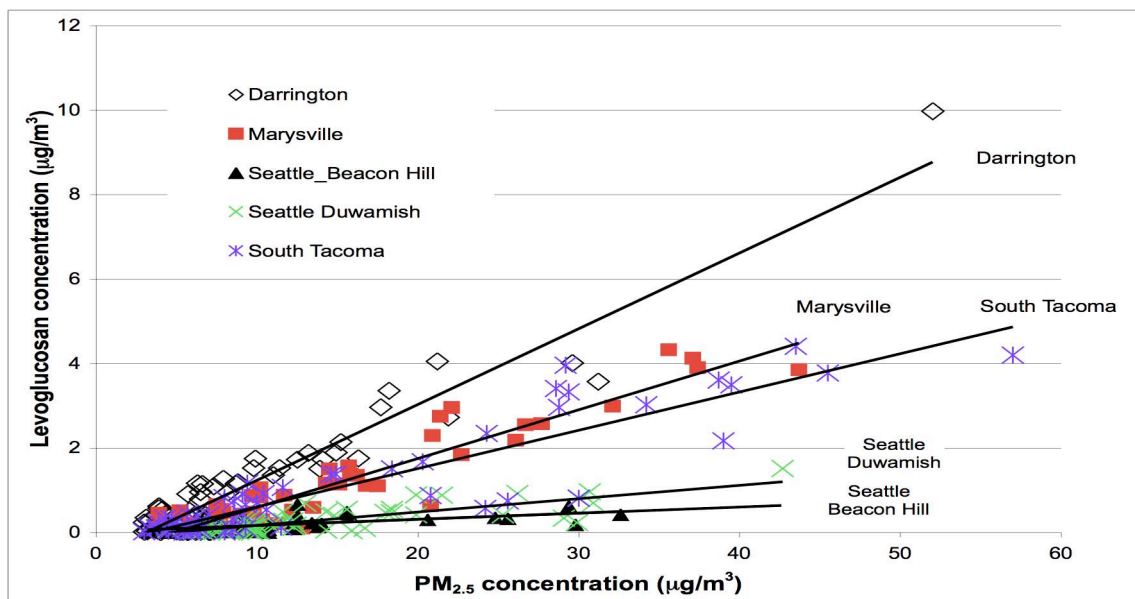


Figure 7: Associations between levoglucosan and PM mass at five monitoring sites in the Puget Sound Airshed.

Figure 7 is a scatter plot that illustrates the associations between $PM_{2.5}$ concentrations and levoglucosan for each of the sites. A relatively strong association between $PM_{2.5}$ and levoglucosan concentrations is seen for the three woodsmoke dominated locations – and furthermore, the slope of the association is similar for these three locations, indicating that levoglucosan constitutes a similar fraction of the $PM_{2.5}$ mass at all three sites. In contrast, the association between $PM_{2.5}$ concentrations and levoglucosan is much poorer at the two Seattle sites that are not woodsmoke dominated. Levoglucosan constitutes a lower and more variable fraction of $PM_{2.5}$ mass at these sites than it does at the other three locations.

Figure 8 shows the ratio of LG to total $PM_{2.5}$ for each of the five sites, grouped by heating and non-heating season. Higher values of the LG/ $PM_{2.5}$ ratio indicate a higher contribution of woodsmoke sources to ambient $PM_{2.5}$. This figure provides a visual ranking of sites based on the relative contribution of woodsmoke to ambient $PM_{2.5}$ at each site. It also clearly distinguishes the high woodsmoke locations (Darrington, Tacoma_South, Marysville) from the low woodsmoke locations (Seattle_Duwamish and Seattle_Beacon Hill). Amongst the three “high woodsmoke” locations, Darrington stands out from the other two sites as having a particularly high LG: $PM_{2.5}$ ratio, especially in the heating season.

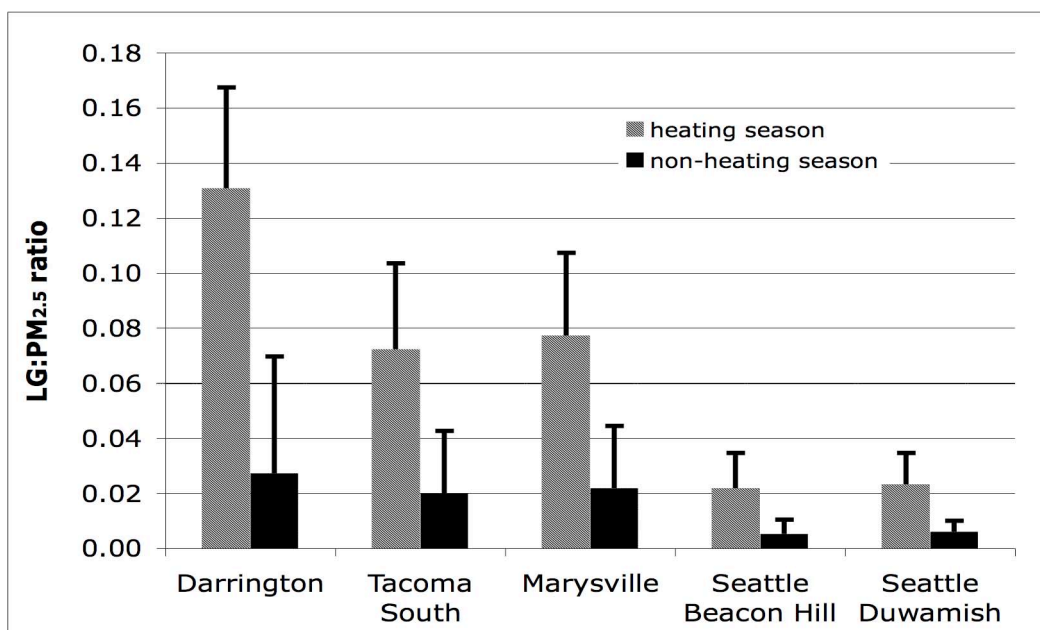


Figure 8: Ratio of levoglucosan to total $PM_{2.5}$ at the five monitoring sites in the Puget Sound Airshed. Higher values of the levoglucosan: $PM_{2.5}$ ratio indicate increased contributions of woodsmoke to ambient $PM_{2.5}$. Error bars represent ± 1 SD.

We used the data from the three woodsmoke-dominated locations (Darrington, Tacoma_South, Marysville) to empirically estimate scaling factors relating levoglucosan concentration to woodsmoke derived $PM_{2.5}$ mass. Firstly, we selected the subset of days with the upper tertile of levoglucosan concentrations at the Darrington, Tacoma_South and Marysville sites – these would be the days where woodsmoke was anticipated to be

the dominant source of PM_{2.5}. The slope of the regression equation linking levoglucosan to PM_{2.5} mass was calculated, and converted to the weight percent of levoglucosan per unit mass of PM_{2.5} (Table 4). A zero intercept was used, consistent with our assumption that woodsmoke was the dominant source of PM_{2.5} for the dates/locations included in the regression.

Table 4: Empirically derived scaling factors indicating the relationship between levoglucosan and PM_{2.5} mass for woodsmoke dominated periods and locations in the Puget Sound Airshed.

	Average % levoglucosan per $\mu\text{g PM}_{2.5}$	95% confidence interval
Darrington	13.9	12.7-15.2
South Tacoma	9.6	8.6-10.5
Marysville	10.0	9.1-10.7

The scaling factors for South Tacoma and Marysville are identical within the confidence intervals for these data. The two 95% confidence intervals are also narrow ($\pm 1.5\%$) which indicates that levoglucosan forms a consistent fraction of woodsmoke associated PM_{2.5} mass at these two locations, despite the variety of woodburning devices in use at these locations and the geographic and demographic differences between the locations themselves. It is notable that these values are also in agreement with the scaling factor of 9.3% determined from the PMF analysis at Beacon Hill (Figure 2). The scaling factor at Darrington is clearly higher than at the other locations, although not dramatically so. The similarity of these scaling factors would suggest that it is possible to estimate with acceptable accuracy the woodsmoke derived PM_{2.5} concentrations based on measurements of levoglucosan on archived filter samples.

A key assumption in these calculations is that all PM_{2.5} is derived from woodsmoke for the subset of dates and locations included in the analysis for table 4. In the case of Darrington, a small rural community (population 1200) in a valley in the foothills of the North Cascades, this assumption is certainly reasonable. In the cases of Marysville (population 25,000) and South Tacoma (population ~100,000) which are both suburban communities, it is likely that a small but non-negligible proportion of the PM_{2.5} is derived from non-woodsmoke sources. Therefore it is reasonable to believe that the scaling factors listed in Table 4 for Marysville and South Tacoma are biased low, and that the true scaling factors for these locations should be closer to the value reported in Table 4 for Darrington.

Figure 9 summarizes previously reported scaling factors for the relationship between levoglucosan and woodsmoke derived PM_{2.5} mass. Values from the current study are included in this figure for comparison. The scaling factor values in figure 9 obtained from previous studies are all derived from source testing studies with residential woodburning stoves using a variety of fuels (wood types) and burn conditions. The values of the scaling factor determined in the current study are in the mid-range of the values listed in figure 9, and overlap with the range of values published by Fine and Nolte. Ward and co-

workers also reported a levoglucosan to $PM_{2.5}$ scaling factor of 10 ± 2 , for ambient measurements made in Libby, Montana (Ward et al, 2006b).

The confidence intervals surrounding the scaling factors determined in the current study are notably narrower than most of the ranges listed in figure 9. This may be due in part to the relatively high number of measurements used to derive the scaling factors determined in the current study, compared to fewer measurements used to determine the scaling factors from the emission studies. The controlled burn experiments using residential woodstoves have shown that there is substantial variation in the relationship between levoglucosan and $PM_{2.5}$ emissions, due to factors including stove type, fuel type, fuel moisture and combustion conditions. This variability has raised the question whether it would be possible to predict ambient woodsmoke derived $PM_{2.5}$ concentrations with an acceptable level of precision, based on measurement of levoglucosan in archived filter samples.

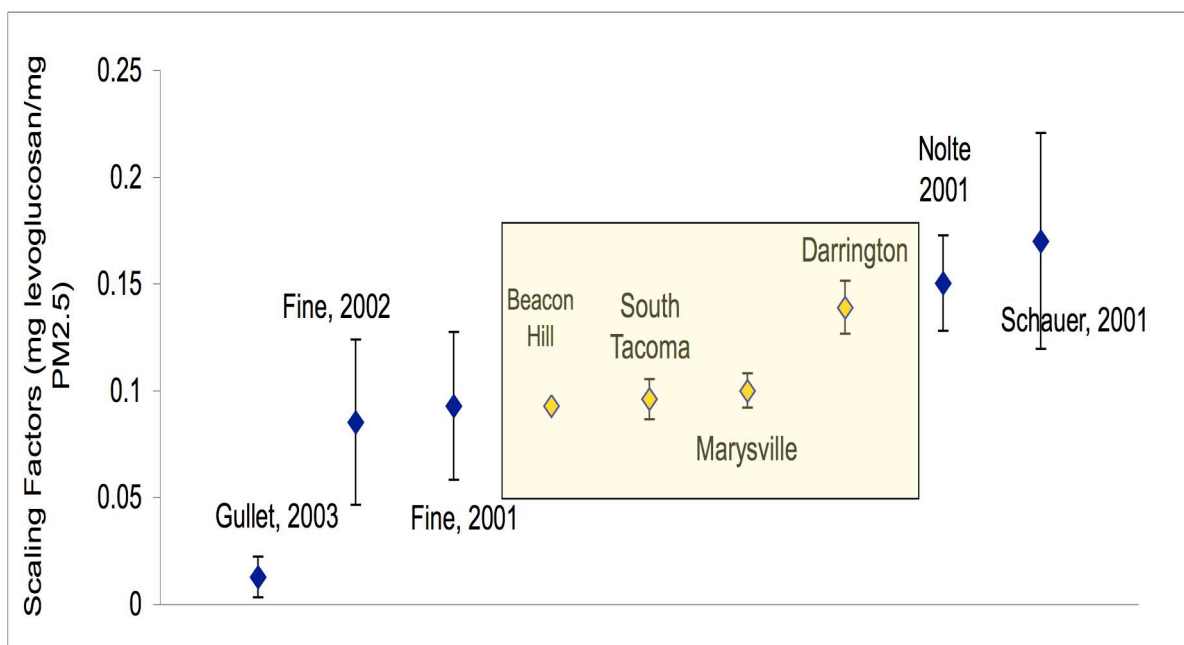


Figure 9: A comparison of scaling factors indicating the relationship between levoglucosan and woodsmoke derived $PM_{2.5}$ mass. The scaling factors highlighted inside the yellow box were determined from ambient measurements at the four Puget Sound sites. Error bars represent ± 1 SD.

The comparatively tight confidence intervals we observed based on the ambient measurements in the current study indicate that for a specific location/community the day-to-day variation in the relationship between woodsmoke derived $PM_{2.5}$ and levoglucosan is sufficiently small that levoglucosan measurements can be used to predict woodsmoke derived $PM_{2.5}$ concentrations with sufficient accuracy and precision to provide useful guidance for air quality managers.

Figure 10 provides an example of how the levoglucosan to $PM_{2.5}$ scaling factor can be used to estimate the fractional contribution of woodsmoke to ambient $PM_{2.5}$

concentrations. Based on Table 4, a scaling factor of 13.9% was used to convert levoglucosan to woodsmoke-derived $PM_{2.5}$ concentrations at the Darrington location. For the other four urban locations a scaling factor of 9.63% was used. This value is the arithmetic mean of the scaling factors listed in table 4 for the Marysville and South Tacoma locations, and the PMF derived scaling factor for Beacon Hill (from Figure 2). Consistent with our findings described earlier in this report, woodsmoke constitutes the highest fraction of ambient $PM_{2.5}$ at the Darrington site (94% heating season, 24% non-heating season), with slightly lower contributions to the Tacoma_South and Marysville sites (75% and 80% respectively in the heating season, 19 and 21% in the non-heating season). From Figure 10 we estimate that woodsmoke contributes 23% of $PM_{2.5}$ concentrations at Beacon Hill in the heating season (5% non-heating season).

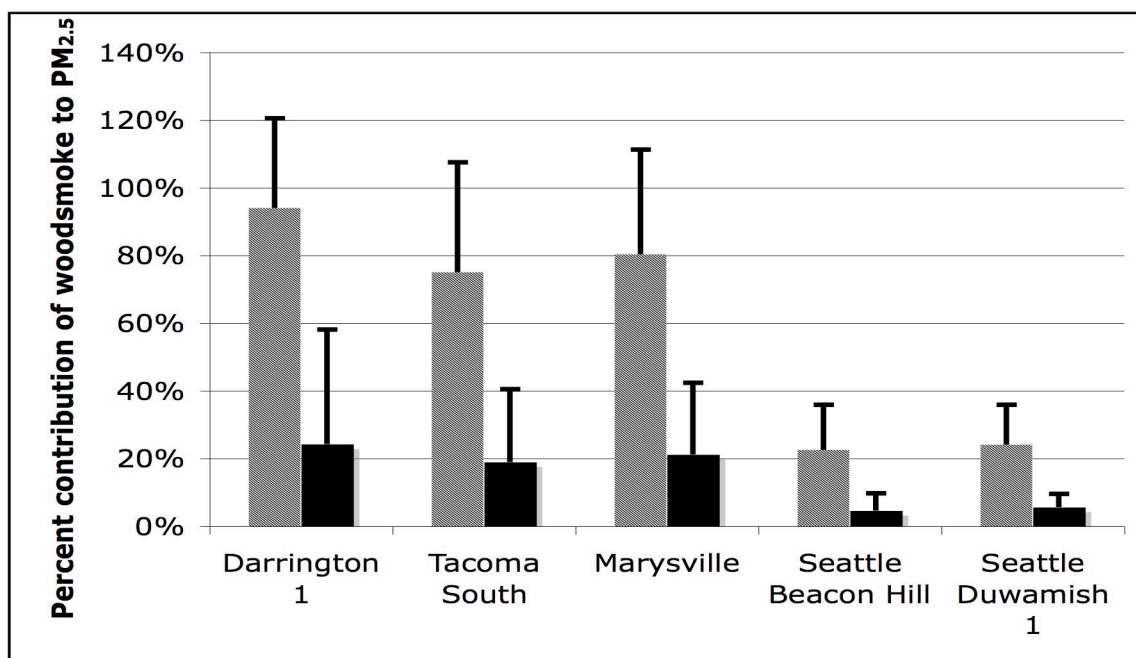


Figure 10: Estimated contribution of woodsmoke to ambient $PM_{2.5}$ at five locations in the Puget Sound Airshed during heating and non-heating seasons. Error bars represent ± 1 SD.

QA/QC

Performance based validation of all chemical assays was undertaken as part of this project. Blank filters were analyzed with each batch of environmental samples to ensure minimal contamination of the assay occurs in the laboratory. Spiked filter samples were also analyzed with each batch of environmental samples in order to assure accurate calibration of the analytical equipment and acceptable performance of the assay. Eight point calibration curves were run at the start and the end of each sample batch to ensure the GC/MS system was appropriately calibrated. Calibrants were re-analyzed periodically throughout the sample analysis sequence to ensure stability of the instrument response.

A stable-isotope-labeled levoglucosan analog (d7-levoglucosan) was added to each filter sample prior to extraction in order to monitor analyte recovery through the assay.

Anhydroheptulose was added to each extract prior to derivatization in order to monitor the efficiency of the derivatization reaction in each sample. d8-Acenaphthalene was added to each extract as an internal standard prior to GC/MS analysis, and used for relative-area quantification of levoglucosan and d7-levoglucosan. For any samples with levoglucosan concentrations outside of the range of the calibrations solutions, the samples were diluted by an appropriate amount and re-analyzed.

For analysis of filters from the five air monitoring sites, order of filter extraction and analysis for filters from four of the locations was randomized to ensure no analytical bias was introduced into the data associated with variation in assay performance over time. Filters from the Beacon Hill site were not included in this randomization procedure because the Beacon Hill filters were not available to be analyzed until towards the end of the project period. Consequently, the Beacon Hill filters were analyzed as a single group.

Conclusions

The primary aim of this study was to evaluate the utility of levoglucosan as a chemical marker to identify and quantify particulate air pollution coming from wood burning.

We used an organic extraction procedure followed by derivatisation and GC/MS analysis for the determination of levoglucosan in filter samples. This procedure, which we have previously published and validated was reproducible and provided sufficient sensitivity to reliably detect and quantify levoglucosan in single 24 hours partisol filters – even during the summer months when woodsmoke PM was low, and at locations that were not dominated by woodsmoke derived PM.

Levoglucosan was measured on Teflon filters collected at the Beacon Hill air quality monitoring site in Seattle. The levoglucosan concentrations were regressed against *estimates* of woodsmoke derived PM_{2.5} mass generated from a PMF model. The correlation between these two variables was 0.83, indicating a high degree of association between measured levoglucosan concentrations and *estimated* woodsmoke-derived PM_{2.5} mass. From the Beacon Hill data we calculated that levoglucosan constituted 9.3% of woodsmoke derived PM_{2.5} mass.

To investigate spatial variation in woodsmoke concentration in the Puget Sound Airshed, levoglucosan was measured on 300 Teflon filters collected from five air quality monitoring sites. We found that levoglucosan concentrations were relatively high at the three suburban/rural sites (Darrington, Marysville, Tacoma South) that were expected to be heavily impacted by wintertime use of woodstoves for residential heating. In contrast, levoglucosan concentrations were 4-5 fold lower at the two urban Seattle sites where non-woodsmoke sources of PM_{2.5} were anticipated to be more important. At all locations levoglucosan concentrations were about 10-fold higher in the heating season (October to February) compared to the non heating season.

Based on the levoglucosan measurements and site characteristics, we selected 90 days from the three high-woodsmoke sites where we were confident that woodsmoke was the dominant source of PM_{2.5}. Using data from these locations and time periods we calculated values for the scaling factor that relates levoglucosan to woodsmoke-derived PM_{2.5} mass. We determined that levoglucosan constituted between 9.6-13.9 percent of

PM_{2.5} mass at these three locations on days when woodsmoke was the dominant source of PM_{2.5}. The confidence intervals surrounding these scaling factors were acceptably narrow, suggesting measurements of levoglucosan can be used to predict concentrations of woodsmoke-derived PM_{2.5} with acceptably accuracy and precision. The values of the scaling factor that we derived from ambient measurements were towards the midrange of values reported in the scientific literature based on emissions testing of residential woodstoves under controlled laboratory conditions. Based on a PMF source apportionment of PM_{2.5} samples collected at Beacon Hill between 1996-1999 we obtained a scaling factor of 9.3% for Beacon Hill, which is in good agreement with the scaling factors obtained from analysis of PM_{2.5} samples collected at the Marysville and South Tacoma sites in 2004-2006. However, the scaling factor determined for the rural site (Darrington) was about 40% higher than the values for the urban/suburban locations. This observation indicates that there may be important site-specific differences in the values of the levoglucosan to woodsmoke-PM_{2.5} scaling factor. Useful questions to address in future studies across multiple airsheds would be to determine the extent of within and between region variability in the levoglucosan to woodsmoke-PM_{2.5} scaling factor; to determine suitable regional and/or national values to use for the scaling factor, and to determine the significant or the error or imprecision that would be introduced by using regional/national scaling factors instead of community-specific values.

In conclusion, the studies described herein confirm previous reports that levoglucosan is an effective tracer for woodsmoke derived PM_{2.5}. Furthermore, the current studies indicate that measurements of levoglucosan made on PM_{2.5} filters (including archived samples) can be used to estimate the concentration of woodsmoke derived PM_{2.5} at specific locations, and hence to determine the fractional contribution of woodsmoke to ambient PM_{2.5} concentrations.

Acknowledgements

The authors wish to thank Neil Frank at USEPA's OAQPS and Mike Gilroy at PSCAA for their thoughtful discussions and guidance of this project. We also thank Kathy Himes at PSCAA for the woodstove use maps included in this report, and Timothy Larson and Bethany Katz at the University of Washington for assistance with the PMF model.

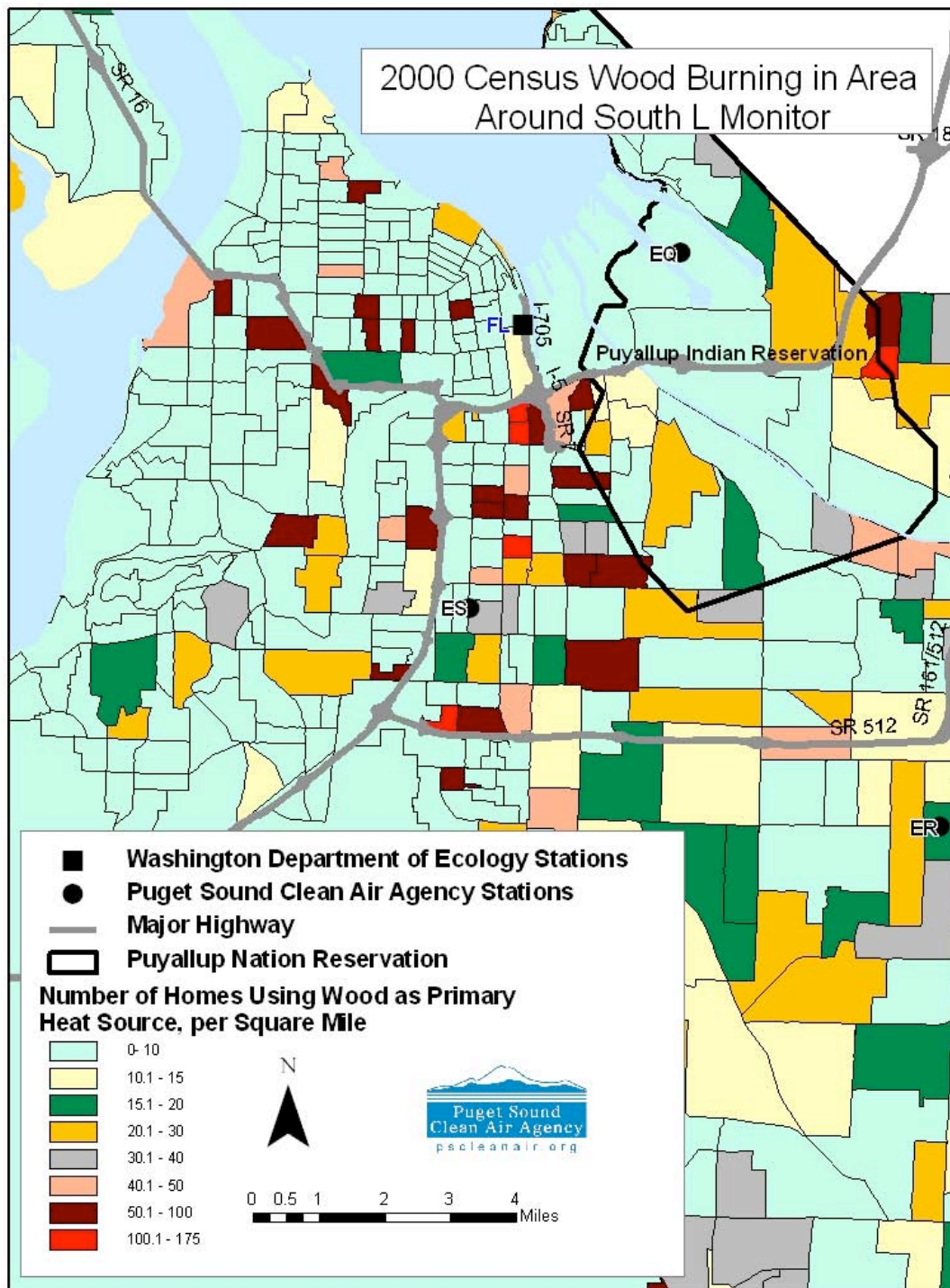
References

- Fine, P. M., G. R. Cass, et al. (2001). "Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States." *Environ Sci Technol* 35(13): 2665-75.
- Fine, P. M., G. R. Cass, et al. (2002). "Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the Southern United States." *Environ Sci Technol* 36(7): 1442-51.
- Goswami, E., T. Larson, et al. (2002). "Spatial characteristics of fine particulate matter: Identifying representative monitoring locations in Seattle, Washington." *Journal of the Air & Waste Management Association* 52(3): 324-333
- Gullett, B. K., A. Touati, et al. (2003). "PCDD/F, PCB, HxCBz, PAH, and PM Emission Factors for Fireplace and Woodstove Combustion in the San Francisco Bay Region." *Environmental Science and Technology* 37(9): 1758-1765
- Hays, M. D., C. D. Geron, et al. (2002). "Speciation of gas-phase and fine particle emissions from burning of foliar fuels." *Environmental Science & Technology* 36(11): 2281-2295.
- Katz, B. (2003) "Estimating the contribution of woodsmoke to fine particulate matter in Seattle using levoglucosan as a molecular tracer." M.S. Thesis, University of Washington
- Larson, T., Gould, T., Simpson, C.D., Claiborn, C., Lewtas, J., Wallace, L., and Liu, L.J.S. Source apportionment of Indoor, Outdoor and Personal PM_{2.5} In Seattle, WA using positive matrix factorization. **2004** *J. Air Waste Manage. Assoc.*, 54, pp1175-1187
- Maykut NN, Lewtas J, Kim E, Larson TV. Source apportionment of PM_{2.5} at an urban IMPROVE site in Seattle, Washington. *Environ Sci Technol.* **2003** 37(22):5135-42.
- Nolte, C. G., J. J. Schauer, et al. (2001). "Highly polar organic compounds present in wood smoke and in the ambient atmosphere." *Environ Sci Technol* 35(10): 1912-9.
- Schauer, J. J., M. J. Kleeman, et al. (2001). "Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood." *Environ Sci Technol* 35(9): 1716-28.
- Simpson, C.D., Katz, B.S., Paulsen, M., Dills, R.L., Kalman, D.A. **2004** Determination of levoglucosan in atmospheric fine particulate matter. *J. Air Waste Manage. Assoc.*, 54, pp 689-694
- Ward, T.J., Hamilton, R., Dixon, R.W., Paulsen, M., Simpson, C.D. **2006** Characterization and evaluation of woodsmoke tracers in PM: Results from the 2003 Montana Wildfire Season, *Atmos. Environ.* 40:7005-7017
- Ward, T.J., Rinehart, L.R., Lange, T. **2006b** The 2003/2004 Libby, Montana PM_{2.5} source apportionment research study, *Aerosol Sci. Technol.* 40:166-177

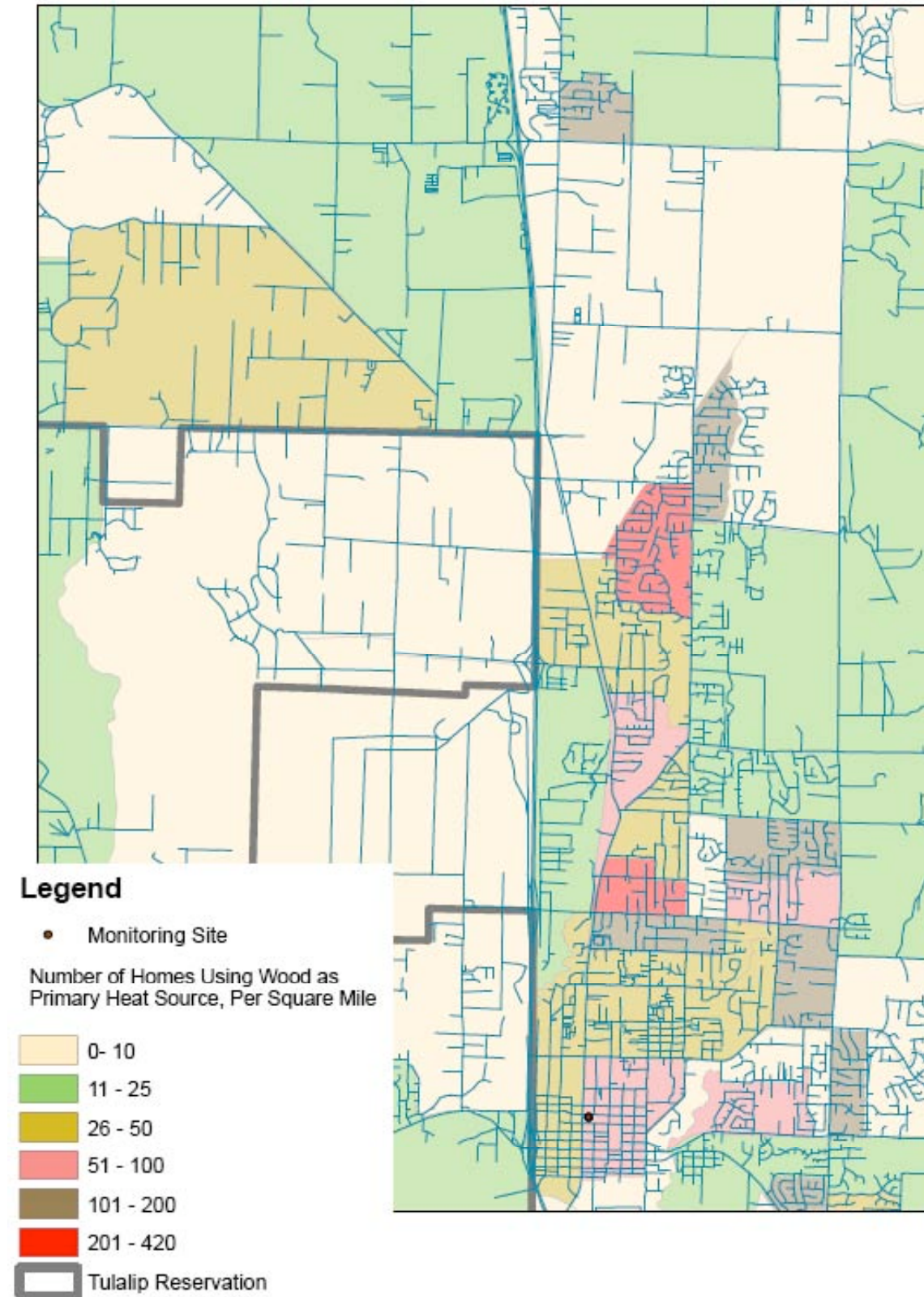
Appendices

1. Woodstove use maps for South Tacoma and Marysville air monitoring sites
2. Standard operating procedures for filter extraction, derivatization and analysis
3. Excel Table listing site, date, PM conc and LG conc

South Tacoma Number of Homes Using Wood as a Primary Heating Source Per Square Mile, 2000 Census



North Marysville Number of Homes Using Wood as a Primary Heating Source Per Square Mile, 2000 Census



**STANDARD OPERATING PROCEDURE (SOP)
FOR EXTRACTION OF LG**

Prepared by:		Date:	
Revised by:	Jacqui Ahmad	Date:	8/22/03
Revised by:	Michael Paulsen	Date:	10/10/03
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Reviewed by:	Jacqui Ahmad Research Technologist	Date:	
Approved by:	Chris Simpson Assistant Professor	Date:	

Standard operating procedures for the extraction of Levoglucosan on Teflon filters

This document describes the standard operating procedure for the extraction of anhydro-sugars (levoglucosan) in atmospheric fine particulate collected on Teflon filters. During method development we have identified potential problems related to analyte losses to unsilanized glassware and volatilization losses of standard compound,. Be aware of these concerns during sample preparation, and endeavor to minimize problems by using silanized glassware. Minimize volatilization losses by storing samples, standards and extracts in the freezer in F455 when they are not in use and ensure that all sealed containers (GC vial, headspace vials) are properly sealed.

Note also that expected levels of many of these analytes are less than 10 ng/sample. To prevent contamination, all equipment and supplies used in the assay must be thoroughly cleaned, and should not be mixed with general lab supplies, remembering that lab glassware has been used to synthesize gram quantities of the analytes of interest.

Supplies:

1. Silanized glassware: 40mL headspace vials, 50mL turbovap tubes, 1.5mL amber GC vials and GC vial micro inserts.
2. Custom built stainless steel/Teflon filter cutter.
3. Aluminum foil (used to line work surfaces).
4. Various sized micro dispenser pipettes and corresponding silanized tubes.
5. Silanized disposable glass Pasteur pipettes (5 3/4" & 9 in).
6. Headspace vial caps and Teflon lined septa.
7. 13mm, PTFE syringe filters, pore size 0.45µm.
8. Plastic, disposable, 3cc, luer-lok tip syringes.

Preparation:

1. All glassware which is in contact with the sample or sample extract must be silanized prior to use. See the silanization SOP for specific instructions on glassware preparation. Glassware may be used three times or less depending on cleanliness before resilanization should take place.
2. All glassware must be tripled rinsed with Ethyl acetate (EtOAc) and dry before each use.
3. **Extraction solvent:** Ethyl acetate with 3.6mM Triethylamine extraction solution must be prepared fresh daily. The Ethyl acetate should be shaken with sodium sulfate prior to preparing this solution, to remove residual water. Add 500µL Triethylamine, HPLC reagent grade (TEA), to 1 liter Ethyl acetate, certified A.C.S. grade (EtOAc). Store the extraction solution in the appropriate bottle top dispenser labeled with preparation date and your initials.
4. Record each unique reagent container id and lot number onto the extraction worksheet. This will aid with troubleshooting if problems arise.

Standard solutions required:

1. Levoglucosan standard, ~100ng/ μ L in EtOAc
2. d₇-Levoglucosan (sugar RSTD), ~100ng/ μ L in EtOAc
3. Anhydroheptulose (sugar derivatization control), ~25ng/ μ L in EtOAc
4. ISTD (10ng/ μ L **TIB** and 60ng/ μ L d8-Acenaphthalene) in EtOAc

Procedure:

1. Obtain clean, silanized 40mL headspace vials; label them with dog-eared ToughTabs (prepare with laser printer). Each individual sample id must be unique.

Extraction Batch Naming Convention Table

Sample id	# Samples	Sample type
BMMDDYY-XX	2	Method blank
DMMDDYY-XX	2	Deuterated spike
FMMDDYY-XX	2	Fortified spike
Environmental samples*	Up to 40	Sample
CMMDDYY-XX	2	100% Control

XX: sequential numerical order (e.g. 01-99).

MMDDYY: month day year of extraction date (e.g. 012403).

** Most of our data analysis involves within-person time-series comparisons. Therefore, to prevent introduction of systematic bias into the data due to changes in instrument and assay performance over time, all samples for a single person of a specific type (e.g. outdoor PM10), should be extracted and analyzed in the same batch. Furthermore using numerical methods (i.e. we don't want to always be running samples in the order day 1 to day 10) should randomize the order in which the samples are extracted and analyzed.*

2. Holding one end of filter by the support ring with tweezers (EtOAc-rinsed), clip the support ring at opposite ends of the filter. Then use the other tweezer to fold the filter. Use one tweezer to stuff folded filter down into headspace vial.
3. Add the appropriate amount of spiking compounds to the appropriate sample id as directed in the spike table below. **Do not add ISTD mix or Anhydroheptulose at this time.** The standards should be spiked directly onto the filter surface (backside of filter). Cap the headspace vial and allow to age for 30 min.
4. Record each unique standard id onto the extraction worksheet. This will aid with troubleshooting if problems arise.

Spike Table

Sample Id	Levoglucosan	d ₇ -Levoglucosan	EtOAc/TEA	Anhydroheptulose*	ISTD mix *
Method Blanks				20 µL	20 µL
Deuterated		20 µL		20 µL	20 µL
Fortified	20 µL	20 µL		20 µL	20 µL
Environmental Samples		20 µL		20 µL	20 µL
100%Control §	20 µL	20 µL	460 µL	20 µL	20 µL

*□STD mix and Anhydroheptulose added as directed below after the extraction and reduction process.

§ 100% Control standard preparation described below.

5. Add 30mL of the freshly prepared extraction solvent (EtOAc with 3.6 mM TEA) to each headspace vial with dispenser.
6. Sonicate the sample extracts for 1 hour. A Styrofoam form is used to hold the headspace vials in place during sonication. The water level in the sonic bath should submerge the extraction solvent level in the headspace vial. Verify the filter is contained within the extraction fluid.
7. Prepare the Turbo Vap II for extract volume reduction.
8. Turbo Vap II instructions: Settings for Turbo Vap II: Endpoint Select = Sensor, Bath Temp. = 45 °C. Make sure the water level in the bath is to the red line. Use purified water from room F-456. Nitrogen tank is located in room F-443 (be sure to close tank valve when finished if you are the last one using it).
9. Label the 50mL turbovap tubes in the same manner as the headspace vials were labeled.
10. Decant solvent into labeled 50mL turbovap tubes trying to leave behind the filter.
 - *Take particular care that the sample ids do not get confused when transferring to the new vessels.*
11. Cap turbovap tubes with EtOAc triple rinsed and dried red caplugs (caps) and transfer sample extracts to F-455.
12. Remove the caplugs from the samples loaded into the TurboVap II.
13. Reduce volume to ~0.5mL. Take special precautions to **not introduce water** into the sample extracts.
14. Recap the turbovap tubes with caplugs and place in rack.
15. Use silanized glass Pasteur pipette (triple rinsed with EtOAc, do not need to wait for these to dry) to rinse apron of turbovap tube should be 6-8 times with extract before transferring.
16. Transfer filter extract to a 3mL PP syringe with a 0.45 mm PTFE/PP syringe filter attached into a labeled silanized 1.5mL amber glass autosampler vial.

- *Make sure that the syringe is over the GC vial before putting the plunger back in, because samples come out using little or no pressure.*
 - *Take particular care that the sample ids do not get confused when transferring to the new vessels.*
17. Add internal standard mix and Anhydroheptulose to all filtered extracts. See spike table above. Cap vial and shake to mix solutions. Store extracts in freezer until day of derivatization.

Preparation of 100% Controls:

1. To each of 2 silanized amber GC vials add the aliquots indicated for each standard and EtOAc as described in the spike table above (ISTD standard and anhydroheptulose are added at this time as well).
2. Cap GC vials and mix for 30 seconds. The vortex mixer works very well for this.

All sample extracts and 100% controls can be stored in F-455, freezer 9. Record the extract storage box id and box grid numbers in the Sample Log Excel Worksheet.

STANDARD OPERATING PROCEDURE (SOP)
FOR DERIVATIZATION AND ANALYSIS OF

LEVOGLUCOSAN ON TEFLON FILTERS

Prepared by:	Jacqui Ahmad Research Technologist	Date:	8/22/03
Revised by:	Mike Paulsen	Date:	5/16/05
Revised by:	Gretchen Onstad	Date:	6/13/08
Revised by:		Date:	
Revised by:		Date:	
Reviewed by:	Mike Paulsen Research Technologist	Date:	
Approved by:	Chris Simpson Assistant Professor	Date:	

Standard operating procedure for the derivatization and analysis of Levoglucosan on Teflon filters

This document describes the standard operating procedure for the derivatization and analysis of levoglucosan in atmospheric fine particulate collected on Teflon filters. During method development we have identified potential problems related to analyte losses to unsilanized glassware, volatilization losses of standard compounds, and chemical degradation of selected analytes. Be aware of these concerns during sample preparation, and endeavor to minimize problems by using silanized glassware and protecting samples, standards and extracts from light as much as possible. Minimize volatilization losses by storing samples, standards and extracts in the freezer in F455 when they are not in use and ensure that all sealed containers (GC vial, headspace vials) are properly sealed.

Note also that expected levels of many of these analytes are less than 10 ng/sample. To prevent contamination, all equipment and supplies used in the assay must be thoroughly cleaned, and should not be mixed with general lab supplies, remembering that lab glassware has been used to synthesize gram quantities of the analytes of interest.

Supplies:

9. Silanized glassware: GC vial micro inserts.
10. Crimp top amber GC vials.
11. Various sized micro dispenser pipettes and corresponding silanized tubes.
12. Aluminum foil (used to line work surfaces).

Preparation:

5. **Derivatization agents:**
 - i. MSTFA + 1% TCMS, Pierce Chemical Co. #48915
 - ii. Pyridine, 99.9%, HPLC grade, Aldrich #27,040-7

Derivatization:

1. Locate the extracts prepared according to the SOP Filter Extraction. Sample and QC extracts are stored in F-455, freezer 9. The extract box id and box grid numbers are located in the Woodsmoke Sample Log (G5/ws data/Sample Tracking/Sample Entry Logs).
2. Derivatize a new calibration curve with each sample batch to be analyzed by GC/MS. Filter calibration standards are stored in freezer 5 located in F-455.
3. Allow extracts and calibration standards to come to room temperature.
4. Refer to the sample extraction log sheet to determine if pertinent information is recorded about the individual extracts. Verify the addition of ISTD to the sample and QC extracts.
5. Place a silanized glass insert into an unsilanized amber crimp-top GC vial.
6. Label each GC vials with LG (indicating Levoglucosan preparation), the unique sample id or calibration standard id and the date.

7. For each calibrant aliquot 500 μ L of into a silanized labeled GC vial with out an insert. Add 20 μ L of ISTD mix and 20 μ L of anhydroheptulose (derivatizing control) cap, mix well.
8. Transfer a 50 μ L aliquot of each sample and calibration standard to the silanized glass insert.
 - *Take particular care that the sample ids do not get confused when transferring to the new vessels.*
9. Add 50 μ L of MSTFA + 1% TCMS and 10 μ L of Pyridine to the 50 μ L extracts and calibrants.
10. Cap vial and mix well with vortex mixer (5 seconds of vortex at highest setting is adequate).
11. Allow extracts and calibrants to derivatize overnight in the dark (6 hour minimum).

Instrumental Analysis:

1. Analyze by GC/MS using internal standard calibration. Typically, the 5971 MSD is used for this analysis. LEVSPLSS.M is current method.
2. Gas chromatographic conditions:
 - a. Inlet
 - i. Septa: Thermolite, 11 mm, Restek #20364.
 - ii. Liner: Splitless with fused-silica wool, 4.0 mm i.d., Restek #22401
 - iii. O-ring: Viton, Restek #20377
 - iv. Seal: gold-plated, 0.8 mm, Restek #21318
 - v. Carrier: He
 - vi. Pressure program: Constant Flow at 0.77 ml/min (10 psi at 150 C)
 - vii. Temperature: 250°C
 - b. Column: RTX-5sil ms, 30m, 0.25 mm i.d., 0.25 μ m film thickness, Restek #12723
 - c. Temperature program:
 - i. Initial temperature, 80°C
 - ii. Initial time, 2 min
 - iii. Rate, 20 deg/min
 - iv. Final temperature, 255°C
 - v. Final time, 5 min.
 - vi. Run time 15.75 min.
 - vii. Oven equilibration time, 0.5 min.
 - viii. Transfer line, 280°C
3. Mass spectrometer conditions:
 - a. Mode: SIM
 - b. Solvent delay: 4.5 min
 - c. Resolution High for all groups
4. Data Analysis Parameters:
 - a. Mode: SIM
 - b. Solvent delay: 5 min
 - c. Integration: See Table VI-IV
 - d. Resolution High for all groups
 - a. Group 1

- i. Start time: 5.00
- ii. Plot 1 189, Plot 2 189
- iii. Dwell, 20 for all masses
- iv. Masses 189
- b. Group 2
 - i. Start time: 8.50
 - ii. Plot 204, Plot 204
 - iii. Dwell, 20 for all masses
- e. Masses 204,206,333,339
- f. Deuser Macro: See Appendix I

1. Calibration

- a. Mode: Internal Standard using triisopropylbenzene
- b. Calibrants.
 - i. See Table VI-I. Individual stock solution is prepared in ethyl acetate at approximately 470 $\mu\text{L/mL}$ for levoglucosan. Individual stock solution is prepared in ethyl acetate at approximately 380 $\mu\text{L/mL}$ for d_7 -Levoglucosan. These are combined (volumes in Table VI-I) and diluted in ethyl acetate to give Standard 25 (approximately 25 $\mu\text{L/mL}$). Ethyl acetate is reagent grade.
 - ii. Prepare calibrants by dilution of Standard 25 with ethyl acetate according to Table VI-II.
 - iii. Store in -20°C freezer 5 in F-455.
 - iv. Do not reuse calibrant after they have been punctured and sat overnight at room temperature.

2. Sequences

5. Sequences

- a. The naming convention for a sequence is IIMMDDYY.s, where II is two character initial of the analyst, MM is two digit month, DD is two digit day and YY is two digit year.
- b. A new directory must be created to store the data. Use the same naming convention for the sequence (IIMMDDYY).
- c. A solvent blank is analyzed at the beginning of the sequence to insure the system is clean.
- d. Calibrants are analyzed from low to high concentration, starting with the Zero standard.
- e. A midlevel concentration calibrant is reanalyzed after every ten injections followed by a solvent blank.
- f. Two solvent blanks are analyzed after the highest concentration calibrant is analyzed.
- g. Samples are then analyzed, randomized with respect to collection time. All of an individual subject's samples should be run within a single sequence.
- h. Blank QC samples are analyzed.
- i. Other QC samples (deuterated, fortified, 100% control) are analyzed last.

Method Performance:

Note: these parameters will vary depending on current stock concentrations of standards.

Table VI-I. Calibrant Stock and Standard 25 Preparation.

Chemical	Source	Receipt or Syn. Date	Chemical Purity	Cat. # or Isotopic Purity	Stock Solution	Stock Conc. ($\mu\text{g/ml}$)	Corr. Stock Conc. ($\mu\text{g/ml}$)	Corr. Std. 25 Conc. ($\mu\text{g/ml}$)	Vol. (μl) into 4 ml
Compounds									
Levoglucozan						468	468	25	212
d ₇ -Levoglucozan						383	383	25	261

Table VI-II. Preparation of Calibrants.

Conc. ($\mu\text{g/ml}$)	Source	Volume used of source (ml)	Final Volume (ml)
25	25	4	4
10	25	1.6	4
5	10	2.0	4
2.5	5	2.0	4
1.0	2.5	1.6	4
0.5	1.0	2.0	4
0.25	0.5	2.0	4
0.1	0.25	1.6	4
0.05	0.1	2.0	4
0	Ethyl acetate	0	4

Table VI-III. Calibrant Stock and Standard 25 Preparation.

Chemical	Source	Receipt or Syn. Date	Chemical Purity	Cat. # or Isotopic Purity	Stock Solution	Stock Conc. ($\mu\text{g/ml}$)	Corr. Stock Conc. ($\mu\text{g/ml}$)	Corr. Std. 25 Conc. ($\mu\text{g/ml}$)	Vol. (μl) into 4 ml
Compounds									
Triisopropylbenzene									
Anhydroheptulose									

Table VI-IV. Integration parameters.

Chemical	Type	Ret. Time (min)	Target ion (m/z)	Confirmation ion (m/z)	Integration Events File
Triisopropylbenzene	ISTD	7.23	189		events.e
d ₇ -Levoglucozan	RS	9.51	339	206	events.e
Levoglucozan	A	9.53	204	333	events.e
Anhydroheptulose	RS	10.68	204	333	events.e

A, Analyte; RS, Recovery standard; ISTD, Internal standard.

**STANDARD OPERATING PROCEDURE (SOP)
FOR LEVOGLUCOSAN DATA PROCESSING**

Prepared by:	Jacqui Ahmad Research Technologist	Date:	8/22/03
Revised by:	Mike Paulsen	Date:	8/5/04
Revised by:	Gretchen Onstad	Date:	6/13/08
Revised by:		Date:	
Revised by:		Date:	
Reviewed by:	Mike Paulsen Research Technologist	Date:	
		Date:	
Approved by:	Chris Simpson Assistant Professor	Date:	

Standard operating procedure for Levoglucosan data processing.

In order to ensure that Levoglucosan data from multiple data sets is handled consistently, and to facilitate efficient processing and use of Levoglucosan data by multiple individuals, This SOP was prepared to streamline Levoglucosan data processing.

Note that it is important to ensure that each time the GC/MSD#2 system is used, the hours of use are logged on the sheet attached to the instrument, so that instrument time can be charged appropriately.

Setup and execute data acquisition on GC/MSD#2:

After samples have been derivatized:

1. Activate the MS-ONLY Top icon if not already on the screen.
2. From the Sequence drop down menu select 'Edit Sample Log Table'.
3. Fill in the five cells for each sample line with the appropriate information.
Sample Type: Will be designated as Sample for all vials whether they are calibrants, QC samples or environmental samples.
Vial: The position the vial will be placed on the auto-sampler tray from 1 to 100.
Data File: Leave blank.
Method: The acquisition method to be used. If you highlight this cell and press 'Shift?' the method directory will be brought up on screen.
Sample Name: The unique sample identifier is entered here.
To exit 'Edit Sample Log Table' click OK.
4. From the Sequence drop down menu select 'Save'.
You will be asked to 'save as'. Naming convention: XXMMDDYY, XX= your initials, MM = month, DD = day, YY = year (e.g. JA032703).
5. Load sample vials onto the auto-sampler tray. Verify the sample vials are placed in the correct auto-sampler cup indicated in the sample sequence.
6. Check for adequate solvent (EtOAc) volume in the auto-sampler solvent vials. Also check that the waste auto-sampler vials are empty.
7. Check the auto-sampler syringe. Verify it is clean and the plunger moves freely. Clean syringe with solvent and if necessary replace the syringe with a new one.
8. From the Sequence drop down menu select 'Run'.
Select 'Full Method' for analytical runs.
Enter your initials for Operator Name.
Modify the Data File Directory with your current sequence name.
Select 'Run Sequence' to activate the start of the analytical sequence.

Chromatography review and quantitative calculations using Chemstation

1. In “Data Analysis” view within Chemstation, load the previous levoglucosan data analysis method. Data analysis methods for levoglucosan are identified by the naming convention “LGMMDDYY”. This method will be used as a template for creating a new data analysis method containing the calibration results from the current analytical sequence.
2. Save the data analysis method as “LGMMDDYY”, with MMDDYY matching the sequence name and data file subdirectory.
3. Replace the old calibration results with the new results from the sequence being processed:
 - a. Update retention times for each analyte in the “Edit Compounds” screen.
 - b. Load the high standard.
 - c. Select “Calculate”. Close the report that opens on the screen.
 - d. Select “Q Edit” and inspect the integrations of each peak. Exit and save the changes.
 - e. Do not print the report at this time because the calibration update has not been completed.
 - f. Under “Calibrate”, select “Update”, then “Update One Level”. Change the level number so the current calibration standard matches the table [typically, level 1 is the STD 10, level 2 is STD 5, etc.]. Select “Replace” and then select “Update”.
 - g. Repeat this process for all levels in the calibration table.
 - h. Save the method and proceed to reviewing, quantifying and printing reports for each standard and sample of the sequence.
4. Starting at the beginning of the sequence, “Calculate”, “Q Edit” and “Generate Report” for each sample.
5. Under “Generate Report”, report type should be “Detailed”. This will print quantitative results and SIM plots.

Chromatogram Integration Review

1. For each individual sample analysis a hardcopy printout of the SIM chromatograms was previously created during the “Generate Report” step above.
2. Check integrations of all peaks in all the printed chromatograms. Manually re-integrate peaks where necessary using the Q Edit function in Chem Station. It is not necessary to repeat the “Calculate” step of the data processing.
3. Exit Q Edit and save the changes.
4. Either hand-draw these corrections on the printout using a colored pen or re-print the report with the edited integrations and discard the original printout.

Data output file transfer from GC/MSD#2 to desktop PC:

Data transfer from the GC/MSD#2 is accomplished by compiling a database output file and then saving it onto a floppy disk. The floppy disk is used to transfer the output file to another PC.

1. In Data Analysis, go to “Quantitate” then “Custom Reports” then select “Create New Database”. Set up the database file in the following format:
 - Header
 - Sample Name
 - All Compounds
 - Compound Information
 - Ret Time
 - Target Response
 - Amount
 - Manual Integration
2. There should be 36 columns resulting from this format. Select “OK”.
3. When prompted “Do you want to update...”, select “Yes”.
4. To select the files to be compiled, highlight files in the “Data File Name” field then click on the “--->” button.
5. Select “OK” and the database file will be built.
6. When prompted to “Save As”, save in C:\hpchem\custrpt\LG Database Files. After saving, cancel out of the next two screens to return to Data Analysis screen.
7. In Windows Explorer, copy the file created (XXMMDDYY) to a floppy disk and then take the disk to a desktop PC.
8. Copy the file from the floppy disk to desktop PC.
9. Open the database output file in Excel. This file will have an extension “.CRD”.
10. Save the file as an Excel file (.XLS extension).
11. Insert a new worksheet into the Excel file. Copy the data from the first worksheet into the new worksheet using the *paste/special/values* options. Rename the new worksheet “Edited”.
12. Arrange the data in the “Edited” worksheet to the format of the example worksheet included in this SOP.
13. Save the Excel file and print out hard copies of the Edited worksheet for filing with the data printouts.

Filing hard copies

Each sample set should have its own folder, labeled with the sequence name (XXMMDDYY) and “Levoglucosan”. In the folder, there should be (in order):

1. GC/MSD#2 sequence table printout.
2. Copy of the bench-sheet.
3. One printout of the “Edited” worksheet from the Excel data file.
4. A printed copy of the GC/MS data analysis method “LGMMDDYY”, that contains the calibration information.
5. GC/MS chromatograms for each sample.

Data Review and Compilation:

1. Calculate spike recoveries for D7-levoglucosan for all environmental samples and “D”, “F”, and “C” control samples.
2. Calculate spike recoveries for levoglucosan for “F” and “C” control samples.
3. Tabulate spike recoveries for TIB and anhydroheptulose for all calibrants and samples. Review these results to determine whether there are any excessively high or low values. [If there are anomalies, troubleshoot individual samples by reviewing the chromatography for interferences or integration errors; check the bench sheets for comments regarding problems or special treatment of these samples.]
4. Compile the reviewed data into compilation spreadsheet that separates environmental samples, calibrants, and QC samples.

**Tabulation of levoglucosan and related measurements for
Puget Sound Air Monitoring Sites**

Data for Darrington Air Monitoring Site

ID	Date	Darrington 1 sampled vol (m3)	Darrington 1 LG (ug)	Darrington 1 LG (ug/m3)	Darrington 1 Pm2.5 Partisol (daily) ug/m3
06263817	7/21/06	24.0	0.33	0.01	6.5
06283807	7/24/06	24.0	0.11	0.00	5.2
06283808	7/27/06	24.0	0.18	0.01	4.0
06283811	8/5/06	24.0	0.64	0.03	6.2
06283829	8/8/06	24.0	0.30	0.01	5.7
06283830	8/11/06	24.0	0.40	0.02	6.2
06303806	8/14/06	24.0	0.13	0.01	5.7
06303807	8/17/06	24.0	0.31	0.01	7.0
06323823	8/20/06	24.0	0.14	0.01	7.1
06323825	8/26/06	24.0	0.48	0.02	5.4
06323827	9/1/06	24.0	0.84	0.03	5.0
07063836	3/3/07	24.0	22.95	0.96	6.5
07063859	3/6/07	24.0	6.40	0.27	3.9
07073814	3/15/07	24.0	9.69	0.40	6.1
07103837	3/21/07	24.0	5.67	0.24	3.0
07103841	3/30/07	24.0	7.38	0.31	7.0
07103867	4/5/07	24.0	0.76	0.03	3.2
07143823	4/20/07	24.0	18.97	0.79	6.5
06343820	9/10/06	24.0	0.41	0.02	3.0
06403818	10/16/06	24.0	8.10	0.34	5.4
06403821	10/22/06	24.0	85.86	3.58	31.2
06403823	10/28/06	24.0	10.02	0.42	6.8
06443813	11/12/06	24.0	10.14	0.42	4.3
06423840	11/18/06	24.0	26.37	1.10	7.3
06463832	11/30/06	24.0	32.61	1.36	11.0
06463846	12/3/06	24.0	65.42	2.73	21.9
06463836	12/9/06	24.0	41.47	1.73	12.5
06483822	12/12/06	24.0	13.76	0.57	3.9
06483824	12/18/06	24.0	96.25	4.01	29.6
06483825	12/21/06	24.0	7.05	0.29	3.9
06503812	12/27/06	24.0	41.39	1.72	14.1
06503815	1/5/07	24.0	28.61	1.19	8.8
06503835	1/8/07	24.0	27.68	1.15	8.7
06523816	1/14/07	24.0	239.37	9.97	52.0
06523817	1/17/07	24.0	42.28	1.76	16.3
07023825	1/23/07	24.0	45.35	1.89	13.2
07023828	2/1/07	24.0	8.50	0.35	3.1
07043831	2/7/07	24.0	36.65	1.53	9.8
07043832	2/10/07	24.0	22.92	0.95	8.2
07043833	2/13/07	24.0	14.98	0.62	3.9
07043834	2/16/07	24.0	9.55	0.40	4.7
07063835	2/28/07	24.0	27.62	1.15	6.6
07383808	9/29/07	24.0	11.16	0.47	4.4
07383810	10/5/07	24.0	12.81	0.53	4.1
07383812	10/11/07	23.9	6.41	0.27	3.3
07383836	10/14/07	24.1	7.30	0.30	6.0
07403804	10/23/07	24.0	28.09	1.17	6.3
07403805	10/26/07	24.0	12.28	0.51	5.8
07403841	10/29/07	24.0	71.27	2.97	17.7
07403842	11/1/07	24.0	36.62	1.53	11.4
07423813	11/4/07	24.0	42.05	1.75	9.9
07423815	11/10/07	24.0	9.76	0.41	3.7
07443819	11/16/07	24.0	21.84	0.91	5.7
07443820	11/19/07	24.0	36.19	1.51	13.9
07463820	11/28/07	24.0	51.38	2.14	15.2
07463821	12/1/07	24.0	45.40	1.89	14.9
07483842	12/8/07	24.0	80.53	3.36	18.2
07503804	12/14/07	24.0	97.30	4.05	21.2
07503846	12/23/07	24.0	30.48	1.27	7.9
07503849	12/26/07	24.0	29.64	1.235	7.7

Data for Marysville Air Monitoring Site

ID	Date	Marysville sampled vol (m3)	Marysville LG (ug)	Marysville LG (ug/m3)	Marysville Pm2.5 Partisol (daily) ug/m3
04063805	3/1/04	24.1	14.27	0.59	13.5
04103803	3/31/04	24.1	9.76	0.40	7.2
04123832	4/27/04	24.1	2.31	0.10	7.5
04163809	5/15/04	24.1	2.94	0.12	10.3
04223816	6/23/04	24.1	0.57	0.02	8.8
04223835	6/29/04	24.1	0.70	0.03	6.6
04263803	7/11/04	24.0	0.35	0.01	6.1
04283814	8/1/04	24.1	0.63	0.03	4.1
04343811	9/6/04	24.1	5.47	0.23	10.2
04343812	9/9/04	24.0	2.08	0.09	4.4
05123827	4/22/05	24.1	1.83	0.08	9.4
05143808	4/28/05	23.6	2.16	0.09	7.7
05163814	5/13/05	24.1	5.00	0.21	11.3
05203829	6/15/05	24.1	0.93	0.04	4.8
05063836	3/5/05	24.0	7.18	0.30	10.3
05103813	3/23/05	24.0	20.17	0.84	10.2
05123804	4/7/05	24.1	5.27	0.22	5.9
05263804	7/15/05	24.1	3.08	0.13	8.7
05283812	8/2/05	24.1	1.25	0.05	5.9
04363829	10/3/04	24.1	15.18	0.63	20.8
04363830	10/6/04	24.1	5.14	0.21	6.2
04403811	10/18/04	24.1	5.96	0.25	4.1
04403812	10/21/04	24.1	10.40	0.43	9.0
04403813	10/24/04	24.1	8.07	0.33	7.6
04403815	10/30/04	24.1	11.27	0.47	7.7
04403834	11/5/04	24.0	92.40	3.85	43.7
04443806	11/14/04	24.0	15.65	0.65	7.5
04463810	11/26/04	24.0	13.07	0.54	7.8
04463812	12/2/04	24.1	61.49	2.55	26.7
04463837	12/11/04	24.0	25.38	1.06	10.2
04483808	12/17/04	24.1	71.33	2.96	22.1
04503809	12/26/04	24.1	21.23	0.88	11.7
04503814	1/7/05	24.0	27.35	1.14	15.1
04503837	1/10/05	24.1	66.22	2.75	21.4
04503838	1/13/05	24.0	2.40	0.10	12.8
05023813	1/25/05	24.0	52.46	2.19	26.1
05023814	1/28/05	24.0	32.52	1.35	16.2
05023815	1/31/05	24.1	11.61	0.48	9.8
05023816	2/3/05	24.0	55.16	2.30	20.9
05063814	2/24/05	23.6	60.78	2.58	27.7
05363812	9/19/05	24.1	0.97	0.04	6.5
05363837	10/4/05	24.0	12.66	0.53	12.2
05363838	10/7/05	24.1	6.62	0.27	7.0
05363840	10/10/05	24.1	11.33	0.47	7.9
05403810	10/19/05	24.1	7.66	0.32	7.7
05403814	10/28/05	24.1	3.02	0.13	3.9
05423807	11/12/05	24.1	10.97	0.45	3.9
05443813	11/18/05	24.1	26.56	1.10	17.5
05443815	11/24/05	24.0	36.16	1.51	14.5
05443834	11/27/05	24.0	28.06	1.17	14.3
05463801	12/6/05	24.0	26.61	1.11	16.8
05463802	12/9/05	24.0	98.98	4.12	37.1
05463821	12/12/05	24.1	72.00	2.99	32.1
05483809	12/15/05	24.0	93.60	3.90	37.4
05483810	12/18/05	24.0	103.74	4.32	35.6
05523812	1/20/06	24.1	12.25	0.51	5.2
05523830	1/23/06	24.0	20.97	0.87	9.7
06023819	2/7/06	24.0	37.72	1.57	15.7
06023830	2/10/06	24.1	44.27	1.84	22.7
06063807	2/25/06	24.0	32.91	1.37	15.8

Data for Tacoma South Air Monitoring Site

ID	Date	sampled vol (m3)	LG (ug)	LG (ug/m3)	Pm2.5 Partisol (daily) ug/m3
04063803	3/1/04	24.0	7.63	0.32	8.5
04103801	3/31/04	24.0	10.99	0.46	5.7
04123829	4/27/04	24.0	1.86	0.08	6.5
04163813	5/15/04	24.0	1.28	0.05	6.3
04223804	6/23/04	24.0	0.41	0.02	8.0
04223824	6/29/04	23.8	0.41	0.02	5.9
04243806	7/11/04	24.0	1.93	0.08	5.4
04263816	8/1/04	24.0	0.32	0.01	8.0
04323818	9/6/04	24.0	2.34	0.10	9.3
04323820	9/9/04	24.0	0.43	0.02	3.0
05143801	4/22/05	24.0	2.90	0.12	11.5
05143803	4/28/05	24.0	0.91	0.04	5.9
05163828	5/13/05	24.0	2.72	0.11	8.4
05203822	6/15/05	24.0	0.62	0.03	4.5
05063832	3/5/05	24.0	9.94	0.41	7.0
05103803	3/23/05	23.7	2.86	0.12	5.8
05103829	4/7/05	24.0	4.19	0.17	4.7
05243830	7/15/05	24.0	1.48	0.06	8.5
05283802	8/2/05	24.0	0.25	0.01	5.5
04363821	10/3/04	24.0	17.90	0.75	25.6
04363822	10/6/04	24.0	2.00	0.08	5.0
04383816	10/18/04	24.0	7.84	0.33	4.7
04383818	10/21/04	24.0	15.69	0.65	9.3
04403801	10/24/04	24.0	17.72	0.74	8.6
04403826	10/30/04	24.0	2.21	0.09	3.4
04403828	11/5/04	24.0	100.66	4.19	57.0
04423816	11/14/04	24.0	83.83	3.49	39.5
04443820	11/26/04	24.0	21.79	0.91	9.1
04463801	12/2/04	24.0	36.15	1.51	18.4
04463828	12/11/04	24.0	3.00	0.13	3.3
04463831	12/17/04	23.9	19.28	0.81	30.0
04483817	12/26/04	24.0	25.51	1.06	11.6
04503827	1/7/05	24.0	22.16	0.92	10.4
04503828	1/10/05	24.0	33.07	1.38	14.9
04503829	1/13/05	24.0	28.00	1.17	9.4
04523815	1/25/05	24.0	52.05	2.17	39.0
05023801	1/28/05	24.0	13.65	0.57	24.2
05023802	1/31/05	24.0	16.72	0.70	10.0
05023803	2/3/05	24.0	32.88	1.37	14.6
05043815	2/24/05	24.0	70.95	2.96	28.8
05343816	9/19/05	24.0	2.91	0.12	4.6
05363828	10/4/05	24.0	10.30	0.43	9.1
05363829	10/7/05	24.0	3.84	0.16	5.7
05383801	10/10/05	24.0	12.85	0.54	10.6
05383817	10/19/05	23.6	4.77	0.20	6.2
05403827	10/28/05	24.0	5.49	0.23	3.9
05423818	11/12/05	24.0	8.05	0.34	4.3
05423821	11/18/05	24.0	20.86	0.87	20.8
05443802	11/24/05	24.0	56.27	2.34	24.3
05443824	11/27/05	24.0	81.65	3.40	28.6
05443831	12/6/05	24.0	105.70	4.40	43.5
05463816	12/9/05	24.0	86.46	3.60	38.7
05463817	12/12/05	24.0	72.60	3.03	34.2
05483801	12/15/05	24.0	90.58	3.77	45.5
05483802	12/18/05	24.0	94.91	3.95	29.2
05523823	1/20/06	24.0	2.45	0.10	3.8
05523824	1/23/06	24.0	19.77	0.82	8.0
06023817	2/7/06	24.0	79.89	3.33	29.4
06043801	2/10/06	23.8	9.09	0.38	6.3
06043818	2/25/06	24.0	40.11	1.67	20.3

Data for Seattle_Duwamish Air Monitoring Site

ID	Date	sampled vol (m3)	LG (ug)	LG (ug/m3)	Pm2.5 Partisol (daily) ug/m3
04063801	3/1/04	24.0	2.18	0.09	9.4
04103802	3/31/04	24.0	2.01	0.08	6.4
04123830	4/27/04	24.0	1.86	0.08	9.5
04163816	5/15/04	24.0	1.50	0.06	8.4
04223809	6/23/04	24.0	0.52	0.02	10.1
04223828	6/29/04	24.0	0.18	0.01	7.0
04243811	7/11/04	24.0	0.67	0.03	6.6
04283828	8/1/04	24.0	0.21	0.01	9.7
04343806	9/6/04	24.0	0.90	0.04	9.9
04343808	9/9/04	24.0	0.48	0.02	6.1
05123824	4/22/05	24.0	1.04	0.04	15.9
05143805	4/28/05	24.0	0.93	0.04	9.5
05163827	5/13/05	24.0	1.37	0.06	14.3
05203825	6/15/05	24.0	0.30	0.01	5.8
05063834	3/5/05	24.0	2.48	0.10	7.4
05103807	3/23/05	24.0	1.32	0.06	6.4
05103833	4/7/05	24.0	1.44	0.06	7.7
05243836	7/15/05	24.0	2.27	0.09	16.7
05283805	8/2/05	23.9	0.11	0.00	8.3
04363824	10/3/04	24.0	5.63	0.23	29.9
04363825	10/6/04	24.0	1.68	0.07	9.7
04403806	10/18/04	24.0	2.66	0.11	8.4
04403803	10/21/04	24.0	4.00	0.17	12.4
04403804	10/24/04	24.0	7.35	0.31	9.1
04403829	10/30/04	24.0	0.93	0.04	6.1
04403831	11/5/04	24.0	36.28	1.51	42.7
04423818	11/14/04	24.0	11.77	0.49	14.3
04443823	11/26/04	24.0	11.61	0.48	11.6
04463804	12/2/04	24.0	13.12	0.55	18.4
04463832	12/11/04	24.0	1.65	0.07	4.5
04463835	12/17/04	24.0	8.01	0.33	29.1
04483819	12/26/04	24.0	7.52	0.31	9.5
04503831	1/7/05	24.0	6.60	0.28	12.2
04503832	1/10/05	24.0	5.58	0.23	11.1
04503833	1/13/05	24.0	4.73	0.20	9.9
05023805	1/25/05	24.0	16.71	0.70	30.9
05023807	1/28/05	24.0	10.02	0.42	19.9
05023808	1/31/05	24.0	6.24	0.26	11.7
05023809	2/3/05	24.0	11.27	0.47	18.0
05063806	2/24/05	24.0	19.62	0.82	30.0
05363803	9/19/05	24.0	0.76	0.03	7.4
05363831	10/4/05	24.0	3.06	0.13	12.3
05363833	10/7/05	24.0	3.99	0.17	9.3
05363834	10/10/05	24.0	9.67	0.40	14.8
05383819	10/19/05	24.0	3.07	0.13	9.7
05403832	10/28/05	24.0	3.01	0.13	9.9
05443803	11/12/05	24.0	5.18	0.22	7.4
05443806	11/18/05	24.0	11.22	0.47	18.4
05443808	11/24/05	24.0	21.31	0.89	19.9
05443827	11/27/05	24.0	16.53	0.69	13.0
05443832	12/6/05	23.7	12.83	0.54	15.6
05463818	12/9/05	24.0	9.97	0.42	25.3
05463819	12/12/05	24.0	22.96	0.96	30.7
05483804	12/15/05	24.0	21.03	0.88	21.5
05483805	12/18/05	24.0	1.77	0.07	7.3
05523826	1/20/06	24.0	4.27	0.18	11.2
05523827	1/23/06	24.0	2.94	0.12	11.0
06023821	2/7/06	24.0	21.98	0.92	26.2
06043804	2/10/06	24.0	2.01	0.08	7.8
06063803	2/25/06	24.0	5.67	0.24	9.8

Data for Seattle_Beacon Hill Air Monitoring Site

ID	Date	sampled vol (m3)	LG (ug)	LG (ug/m3)	Pm2.5 Partisol (daily) ug/m3
04083531	3/1/04	23.7	2.82	0.12	6.8
04123544	3/31/04	24.0	1.20	0.05	5.5
04163543	4/27/04	24.0	0.46	0.02	7.0
04183549	5/15/04	24.0	0.56	0.02	7.5
04243544	6/23/04	23.5	0.24	0.01	9.0
04263543	6/29/04	24.0	0.09	0.00	5.3
04283523	7/11/04	24.0	0.34	0.01	6.0
04303541	8/1/04	24.0	0.09	0.00	10.7
04343545	9/6/04	24.0	0.33	0.01	7.9
04363526	9/9/04	23.8	0.08	0.00	4.2
05153520	4/22/05	24.0	0.48	0.02	9.9
05153526	4/28/05	23.9	0.24	0.01	5.9
05173528	5/13/05	23.6	2.04	0.09	12.3
05233517	6/15/05	24.0	0.17	0.01	4.8
05073535	3/5/05	24.0	2.70	0.11	6.8
05113521	3/23/05	24.0	0.50	0.02	5.5
05133523	4/7/05	23.9	0.82	0.03	5.2
05273520	7/15/05	24.0	1.46	0.06	10.7
05293524	8/2/05	23.9	0.13	0.01	6.0
04383544	10/3/04	24.0	4.46	0.19	29.8
04403529	10/6/04	24.0	1.06	0.04	6.9
04403543	10/18/04	23.8	1.72	0.07	3.9
04423530	10/21/04	23.4	3.11	0.13	9.1
04423534	10/24/04	24.0	6.35	0.26	7.5
04423540	10/30/04	24.0	1.08	0.05	4.2
04443532	11/5/04	24.0	14.89	0.62	29.4
04443542	11/14/04	24.0	6.11	0.25	9.3
04463542	11/26/04	24.0	5.37	0.22	6.4
04483527	12/2/04	23.5	5.25	0.22	13.4
04483538	12/11/04	24.0	1.71	0.07	3.5
04503539	12/17/04	23.7	7.68	0.32	25.6
04503540	12/18/04	24.0	10.08	0.42	32.6
04503548	12/26/04	24.0	4.06	0.17	7.7
04523535	1/10/05	23.1	6.89	0.30	9.0
05023521	1/13/05	23.7	3.30	0.14	7.4
05023534	1/25/05	23.8	8.38	0.35	24.8
05033524	1/28/05	24.0	3.28	0.14	13.8
05033527	1/31/05	23.3	3.15	0.14	7.9
05033530	2/3/05	23.8	5.27	0.22	12.3
05353527	9/19/05	23.5	0.35	0.01	6.2
05373536	10/4/05	24.0	2.20	0.09	7.2
05393516	10/7/05	23.9	3.40	0.14	7.1
05393519	10/10/05	23.9	6.91	0.29	9.3
05413517	10/19/05	24.0	2.41	0.10	7.8
05413527	10/28/05	23.9	2.42	0.10	5.0
05433529	11/12/05	24.0	5.82	0.24	4.5
05453520	11/18/05	23.9	5.01	0.21	14.0
05453526	11/24/05	24.0	10.30	0.43	15.7
05453529	11/27/05	24.0	9.82	0.41	6.8
05473520	12/6/05	23.8	4.33	0.18	10.8
05473524	12/9/05	23.8	15.85	0.67	12.5
05473527	12/12/05	23.6	7.24	0.31	20.6
05493523	12/15/05	24.0	9.61	0.40	12.5
05493527	12/18/05	24.0	0.42	0.02	3.2
06013518	1/20/06	23.9	2.59	0.11	4.6
06013521	1/23/06	23.9	2.29	0.10	4.9
06033523	2/7/06	24.0	11.78	0.49	15.6
06053511	2/10/06	23.7	1.95	0.08	3.2
06073511	2/25/06	24.0	4.02	0.17	7.2