Fine Particulate Matter Source Apportionment Following a Large Woodstove Changeout Program in Libby, Montana

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TECHNICAL PAPER

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ABSTRACT

Before a community-wide woodstove changeout program, a chemical mass balance (CMB) source apportionment study was conducted in Libby, MT, during the winter of 2003–2004 to identify the sources of fine particulate matter ($PM_{2.5}$) within the valley. Results from this study showed that residential woodstoves were the major source, contributing approximately 80% of the ambient $PM_{2.5}$ throughout the winter months. In an effort to lower the ambient $PM_{2.5}$, a large woodstove changeout program was conducted in Libby from 2005 to 2007 in which nearly 1200 old woodstoves were changed out with cleaner burning models. During the winter of 2007–2008, a follow-up CMB source apportionment study was conducted to evaluate the effectiveness of the changeout. Results from this study showed that average winter $PM_{2.5}$ mass was reduced by 20%, and woodsmoke-related $PM_{2.5}$ (as identified by the CMB model) was reduced by 28% when compared with the pre-changeout winter of 2003–2004. These results suggest that a woodstove changeout can be an effective tool in reducing ambient levels of $PM_{2.5}$ in woodstove-impacted communities.

INTRODUCTION

Studies conducted throughout the United States[1–10] and world[11–16] have identified woodsmoke as a major component of ambient $PM_{2.5}$. This is especially true in rural northern Rocky Mountain communities where older model woodstoves are major sources of ambient fine particulate matter ($PM_{2.5}$) throughout the cold winter months.[17–19]

Because of prevalent woodstove usage and severe temperature inversions, Libby, MT, has historically experienced elevated concentrations of ambient $PM_{2.5}$ throughout the winter months. Libby is located in a valley (elevation of 628 m) in far northwestern Montana. The population of Libby is approximately 2700, with nearly 10,000 in the Greater Libby Valley. Even with relatively low $PM_{2.5}$ concentrations during the warmer months, the elevated winter $PM_{2.5}$ concentrations have in the past led to Libby exceeding the annual $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) of 15 $\mu g/m^3$. Before the revised daily NAAQS in 2006, Libby was the only $PM_{2.5}$ nonattainment area west of the Mississippi River and outside of Southern California. A chemical mass balance (CMB) $PM_{2.5}$ source apportionment program conducted during the winter of 2003–2004 identified residential wood combustion (woodstoves) as the major source of $PM_{2.5}$ during the 2003–2004 heating season.[18]

It has previously been demonstrated that aggressive campaigns to replace or remove uncertified, or "dirty," woodstoves can have a substantial impact on local air quality, reducing ambient $PM_{2.5}$ emissions by 60–80%.[20] Small-stove changeout programs have been conducted in Seattle, Spokane, Denver, and Reno (among other communities). The first community-wide changeout was conducted in Crested Butte, CO, in 1989–1990, where 48% of the 406 uncertified stoves were replaced by newer units and another 33% were removed or disabled. This resulted in a 60% reduction in ambient $PM_{2.5}$ during the subsequent winter.[21]

In a 2005 emission inventory conducted by the Montana Department of Environmental Quality,[22] there were an estimated 2360 wood burning devices within Libby. This included fireplaces (no insert), precertified woodstoves, U.S. Environmental Protection Agency (EPA) catalytic certified stoves (phases I and II), EPA noncatalytic stoves (phases I and II), cord wood furnaces, masonry furnaces, and pellet stoves/inserts. Most of these devices were old technology (i.e., uncertified cordwood). From 2005 to 2007, a large woodstove changeout program was

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IMPLICATIONS

Studies have shown that ambient $PM_{2.5}$ resulting from residential wood burning is a major source of $PM_{2.5}$ in northern Rocky Mountain valley communities. Because many of these valley communities are in danger of becoming nonattainment areas for $PM_{2.5}$, strategies are needed to lower the impact of this source on the ambient environment. One such strategy is the woodstove changeout. This manuscript demonstrates the effectiveness of the largest community-wide woodstove changeout ever conducted in the United States.

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carried out in which most high-emitting woodstoves were removed and replaced with new, conventional, EPA-certified woodstoves that met the 1988 EPA certification emissions standards of particulate matter emissions less than 7.5 g/hr for conventional models. The conventional model woodstoves utilize firebox insulation; a longer, hotter gas flow path; and preheated combustion air to yield more complete combustion. Other residences chose not to receive a new woodstove and instead opted for the following heating appliance types: gas stoves/heaters/furnaces, wood inserts, pellet stoves, pellet inserts, pellet furnaces, oil stoves/furnaces, electric heaters, and wood furnaces. At the conclusion of the woodstove changeout program in 2007, nearly 1200 old woodstoves were changed out, modified, or surrendered in an effort to lower the ambient $PM_{2.5}$ during the winter heating season.[23,24]

The Libby woodstove changeout program was the largest ever conducted in the United States. The primary goal of the changeout was to reduce the ambient $PM_{2.5}$ resulting from biomass combustion during the winter months. This manuscript describes the application of CMB source apportionment modeling to determine the reduction in smoke-related $PM_{2.5}$ in the Libby airshed following the changeout. In addition, the effectiveness of a woodstove changeout in lowering ambient $PM_{2.5}$ concentrations in woodsmoke impacted communities is evaluated.

EXPERIMENTAL METHODS
$PM_{2.5}$ Sampling and Analyses
During the winters of 2003–2004 and 2007–2008, a Met One spiral ambient speciation sampler (SASS) collected 24-hr integrated ambient air samples on Teflon, nylon, and quartz filter media. The Met One SASS uses a sharp-cut cyclone with a flow rate of 6.7 L/min. The sampling site was located on the roof of the two-story Lincoln County Environmental Health building in downtown Libby and is considered representative of the surrounding area. For both years, samples were collected every 6 days from November through the end of February following the EPA's fixed sampling schedule. All exposed $PM_{2.5}$ speciation filter samples were sent to Research Triangle Institute (RTI; Research Triangle Park, NC) for analyses.[25] The Teflon filters were analyzed for particle mass by a microbalance, and 48 trace elements were analyzed by energy-dispersive X-ray fluorescence (EDXRF). The nylon filters were analyzed for cations (ammonium, potassium, and sodium) and anions (nitrate and sulfate) by ion chromatography. Carbon components, including elemental carbon (EC) and organic carbon (OC), were measured from the quartz filter using thermal optical reflectance.[25] OC data were not corrected for artifacts (i.e., organic vapor adsorption). In addition to the speciation sampler, several Federal Reference Method (FRM) $PM_{2.5}$ samplers were located at the site. The Teflon filters collected by the FRMs were weighed (pre- and postsampling) at Intermountain Laboratories (Sheridan, WY), providing 24-hr ambient $PM_{2.5}$ mass values throughout both winter sampling programs.

CMB Model
The EPA CMB computer model (version 8 for the 2003–2004 data, and version 8.2 for the 2007–2008 data) was used to apportion the sources of $PM_{2.5}$ in the Libby Valley airshed. The CMB receptor model[26–32] consists of a solution to linear equations that expresses each receptor chemical concentration as a linear sum of products of source fingerprint abundances and contributions. The modeling inputs consisted of ambient $PM_{2.5}$ speciation data (mass, elements, ions, and OC/EC) with associated uncertainties along with $PM_{2.5}$ source information (source profile abundances, or the mass fraction of an analyte in the emissions from each source type).

CMB modeling was conducted on 17 sample days from the winter of 2003–2004, whereas modeling was conducted on 19 sample days from the 2007–2008 sampling program. For consistency, the source profiles used in the 2003–2004 program were also used in the 2007–2008 program. These profiles included those for street sand and road dust, pure secondary emissions, gasoline and diesel exhaust emissions (including multiple profiles representative of different operating conditions and fleet types), tire and brake wear, deicer, wood combustion, meat cooking, and oil combustion. Multiple source profiles for each source were used because source compositions can vary substantially among sources, even within a single source over an extended period of time.

Source profiles were taken directly from SPECIATE 3.2[33] or from previous Missoula Valley (Montana) CMB studies.[17,34,35] Because Missoula and Libby have similar topographies and many of the same sources of $PM_{2.5}$, some of the CMB source profiles developed in past Missoula CMB applications were included in the Libby $PM_{2.5}$ source apportionment program. These include profiles for street sand, diesel train and truck exhaust, deicer, and residential wood combustion (RWC). There were no industrial source profiles loaded into the model because there are no large industrial sources in the Libby Valley.

Concentrations of species found on field/trip blanks were not subtracted (or blank-corrected) from the ambient sample concentrations before the modeling was conducted. For each model run, evaluations of several different combinations of source profiles were made, with the number of chemical species always exceeding the number of source types. In addition, a comprehensive quality assurance/quality control (QA/QC) plan was applied throughout the CMB modeling program to ensure accurate results, including the use of the CMB validation protocol.[36]

Statistical Analyses
$PM_{2.5}$ mass and concentrations of carbon components, selected elements, cations, and anions were compared between the 2003–2004 winter and the 2007–2008 winter using SAS version 9.1 (Cary, NC). General linearized models were constructed for each analyte as the dependent variable to determine if the mean concentrations were significantly different between the two winter periods. The following daily meteorological variables collected on the corresponding air sampling days were evaluated as potential explaining factors for each model: mean temperature, mean wind speed, mean relative humidity (RH),

Table 1. Concentration (μg/m^3) and crude percent change of PM$_{2.5}$ mass and selected analytes from the pre- and post-woodstove changeout in Libby, MT.

	Winter 2003–2004		Winter 2007–2008			
	Number of Sample Days	Average (SD) Concentration	Number of Sample Days	Average (SD) Concentration	Crude Percent Change	*P* Value
PM$_{2.5}$ mass from speciated sampler	17	28.2 (6.4)	19	20.1 (5.0)	−25.6	<0.001
PM$_{2.5}$ mass from FRM sampler	36	27.3 (7.5)	38	21.8 (4.9)	−20.3	<0.05
Elements						
Calcium	17	0.025 (0.016)	19	0.020 (0.013)	−20.0	0.022
Chlorine	17	0.033 (0.025)	19	0.028 (0.020)	−17.7	0.478
Iron	17	0.033 (0.020)	19	0.029 (0.018)	−12.1	0.011
Potassium	17	0.140 (0.042)	19	0.146 (0.041)	+4.3	0.692
Silicon	17	0.050 (0.053)	19	0.033 (0.039)	−33.7	0.016
Sulfur	17	0.223 (0.078)	19	0.176 (0.081)	−22.4	0.083
Zinc	17	0.035 (0.020)	19	0.038 (0.017)	+8.6	0.465
Cations						
Potassium	16	0.118 (0.049)	19	0.146 (0.033)	+23.7	0.057
Ammonium	16	0.398 (0.170)	19	0.344 (0.124)	−13.6	0.315
Sodium	16	0.068 (0.051)	19	0.040 (0.025)	−40.8	0.034
Anions						
Nitrate	16	1.188 (0.448)	19	0.969 (0.323)	−18.4	0.500
Sulfate	16	0.600 (0.186)	19	0.523 (0.248)	−12.8	0.318
EC	17	1.667 (0.512)	19	1.447 (0.630)	−13.2	0.261
OC	17	18.19 (3.90)	19	12.60 (3.43)	−30.7	<0.001

Notes: [a]*P* value for difference between years based on least-squares means after adjusting for meteorological variables as appropriate.

solar radiation, and precipitation. Analytes were log-transformed when necessary to approximate normality.

QA/QC Program

For the Libby sampling program in each of the years, the Montana Department of Environmental Quality maintained and audited the PM$_{2.5}$ FRM and speciation samplers. RTI and Intermountain Laboratories were responsible for analytical QA/QC activities within their respective laboratories. In reviewing all of the PM$_{2.5}$ speciated data measured from the field blanks, there was no indication of artifact contamination measured throughout the winter sampling and analytical programs.

As noted earlier, CMB modeling was conducted on 17 sample days from the winter of 2003–2004, whereas modeling was conducted on 19 sample days from the 2007–2008 sampling program. For the 2003–2004 speciation sampling dataset, there were no data recorded for January 10, 2004 and February 15, 2004 because of sampler malfunction. There were no sampler malfunctions during the winter 2007–2008 program. However, the January 1, 2008 dataset did not provide a statistically valid fit for the modeled sources. Therefore, no CMB run was conducted for this day, and the data were removed when computing the analyte averages for winter 2007–2008.

RESULTS
PM$_{2.5}$ Speciation

For the pre-changeout winter, speciation samples were collected every 6 days between November 11, 2003 and February 27, 2004. For the post-changeout winter, samples were collected every 6 days between November 2, 2007 and February 24, 2008. Table 1 presents the PM$_{2.5}$ mass and the values for the elements, ions, and OC/EC measured in both of the winter studies. Only those species

measured above their respective minimum detection limits (MDLs) as reported by RTI throughout the program are presented because most of the measured analytes were below the sensitivity of instrument detection. The MDLs for the elements, anions, and cations ranged from 0.002–0.030 μg/m^3. The MDLs for carbon components and PM$_{2.5}$ mass were 0.24 and 0.74 μg/m^3, respectively. For the FRM samplers, the MDL for mass was 0.6 μg/m^3.

The two different types of samplers used to measure ambient PM$_{2.5}$ mass at the site yielded similar results, both indicating significant mass reductions following the changeout. Using a Teflon filter in the Met One speciated sampler, PM$_{2.5}$ was gravimetrically determined every 6 days in conjunction with the nylon and quartz filters that were collected. In addition, PM$_{2.5}$ mass was measured every 3 days using FRM samplers. In comparing the values from the speciation sampler for the winters of 2003–2004 and 2007–2008, there was a 26% reduction in ambient PM$_{2.5}$. When using the FRM values, there was a 20% reduction in PM$_{2.5}$ mass.

Most of the selected elements had lower average concentrations in 2007–2008 when compared with 2003–2004, but not all of them were significantly lower. Out of all of the elements measured, sulfur had the highest average concentration in both winter periods, followed by potassium. When comparing the two seasons, silicon gave the greatest reduction (33.7%). Among the ions, ammonium (cations) and nitrate (anions) had the highest average concentrations in both winter periods, with sodium showing a significant reduction over time (41%). The Libby ambient PM$_{2.5}$ is heavily enriched with carbonaceous material, specifically the OC fraction. There was a 31% reduction in the amount of OC when comparing the winter of 2007–2008 with the winter of 2003–2004,

Table 2. Meteorological data during two winter periods.

	Winter 2003–2004		Winter 2007–2008		
Data	Number of Sample Days	Average (SD) Measurement	Number of Sample Days	Average (SD) Measurement	*P* Value
Temperature (°F)	17	29.3 (5.7)	19	27.8 (7.6)	0.51
RH (%)	17	90.9 (6.2)	19	82.2 (9.6)	0.003
Precipitation (in.)	17	0.054 (0.11)	19	0.098 (0.21)	0.42
Wind speed (mph)	17	0.28 (0.32)	19	0.25 (0.32)	0.80
Wind gust (mph)	17	3.8 (2.6)	19	2.7 (2.7)	0.85
Solar radiation (°)	17	52.4 (43.8)	19	50.3 (38.7)	0.87

with only a 13% reduction in EC. Meteorological conditions, including temperature, RH, wind speed, wind gust, and solar radiation (Table 2) were similar between the 2 years, with additional precipitation measured during the winter of 2007–2008 when compared with the winter of 2003–2004.

CMB Model

Table 3 presents the $PM_{2.5}$ sources ($\mu g/m^3$) identified by the CMB models for the 2003–2004 and 2007–2008 winter sampling programs, respectively. Also presented in Table 3 are the source percent contribution to overall $PM_{2.5}$ mass and the corresponding standard errors. The standard error is a single standard deviation, and when multiplied 2 or 3 times, the result may be taken as an upper or lower limit of an individual source's contribution. There is approximately a 66% probability that the true source contribution is within 1 standard error, and approximately a 95% probability that the true contribution is within 2 standard errors of the source contribution estimate.

In total, six source profile types were identified as contributing to the Libby $PM_{2.5}$ in the 2003–2004 and 2007–2008 CMBs. These include street sand, secondary sulfate (SO_4), secondary ammonium nitrate (NH_4NO_3), automobiles, diesel exhaust, and RWC. RWC (woodstoves) was identified as the largest source of $PM_{2.5}$ in the Libby Valley for both studies. For the 2003–2004 study, automobiles were detected by the model on 6 of the 17 days, whereas they were detected on only 3 of the 19 sample days in the 2007–2008 program. Diesel exhaust was detected on 6 of the 17 days in the 2003–2004 study,

whereas it was detected in 7 of the 19 2007–2008 sample days.

There were two secondary aerosols (NH_4NO_3 and SO_4) identified by the CMB model as being "pure secondary sources." Both of these secondary sources were detected in nearly all of the model runs for both years. Street sand was only detected in one model run during 2003–2004, and two times during the 2007–2008 program. It was an insignificant contributor to the Libby $PM_{2.5}$ throughout the winter months. Finally, the unexplained mass (the difference between the actual measured mass and the calculated mass) was consistent between both years. There could be additional area sources and background contributions to airshed $PM_{2.5}$ levels throughout each of the two winters; however, individually they are small.

CMB fitting parameters used to evaluate the validity of source contribution estimates were well within EPA target ranges. Table 4 presents the program average key goodness-of-fit parameters for the Libby CMB and the EPA target ranges for each parameter. Although there were a few cases in which the fitting parameters were outside of the EPA target range, none of these cases were considered invalid, and all of the fits were quite strong. Therefore, the source contribution estimates identified in this project can be considered valid.

As expected, there was a reduction in $PM_{2.5}$ mass when comparing the pre-changeout winter of 2003–2004 to the post-changeout winter of 2007–2008. More specifically, results from the CMB modeling showed that the woodsmoke component of the ambient $PM_{2.5}$ was reduced by 28% over this same time period. These reductions are consistent with results from some of the authors'

Table 3. CMB results ($\mu g/m^3$) ± associated standard errors and percent contributions to overall $PM_{2.5}$ mass per source.

	2003–2004 Libby		2007–2008 Libby CMB		
Source	CMB	Percent Contribution to Overall $PM_{2.5}$ Mass	CMB	Percent Contribution to Overall $PM_{2.5}$ Mass	Percent Difference
Street sand	0.02 ± 0.01	0.1	0.04 ± 0.01	0.2	145
SO_4	0.6 ± 0.1	2.1	0.5 ± 0.07	2.2	−23
NH_4NO_3	1.5 ± 0.2	5.2	1.3 ± 0.1	6.3	−13
Automobiles	2.1 ± 0.8	7.4	0.9 ± 0.3	4.5	−56
Diesel	1.0 ± 0.3	3.6	1.1 ± 0.3	5.3	5
RWC	22.8 ± 3.0	81.0	16.4 ± 2.3	81.3	−28
Unexplained	0.19	0.7	0.03	0.2	−83
$PM_{2.5}$ mass	28.2	–	20.1	–	−25.6

Table 4. Average goodness-of-fit parameters for the 2003–2004 and 2007–2008 Libby CMB studies.

Goodness-of-Fit Parameter	2003–2004 Libby CMB	2007–2008 Libby CMB	EPA Target
R^2	0.98	0.96	0.8–1.00
χ^2	0.16	0.35	0.00–4.0
Degrees of freedom	29	30	>5
Percent mass explained	99.3	100.2	80–120%
T-stat	>2	>2	>2

other studies conducted throughout the Libby changeout. When comparing the concentrations of several ambient polycyclic aromatic hydrocarbons (PAHs) and phenolics measured during the winter of 2004–2005 with the winter of 2007–2008 values, there was a 64% average reduction.[37] Levoglucosan (a well known chemical marker of woodsmoke) levels decreased by 50% when comparing winter 2004–2005 values with winter 2007–2008 levels.[38] The reductions were even more substantial for indoor environments in Libby, where average $PM_{2.5}$ concentrations within 16 homes were reduced by 71% (as measured by TSI DustTraks) when old stoves were replaced with new, EPA-certified stoves.[39]

Before the woodstove changeout, woodstoves accounted for approximately 80% of the ambient wintertime $PM_{2.5}$[18]. Following the changeout, woodstoves still accounted for approximately 81% of the ambient wintertime $PM_{2.5}$, although there was a significant reduction in overall $PM_{2.5}$ mass. These findings are consistent with the results of the authors' PAH sampling program in which normalization of the PAH concentrations to the concentration of naphthalene showed a nearly identical profile in comparing the pre- and post-changeout winters. The profile is essentially the same, regardless of which PAH is used for normalization. The similarity in the profile implies that the PAHs measured during these two seasons result from a consistent emission source, with emissions produced under similar pyrolysis or combustion conditions and aged to a similar extent.[37] Although there has been a significant reduction in $PM_{2.5}$ mass in the ambient air as a result of the woodstove changeout, biomass smoke emissions still are the major source within the Libby Valley.

In addition to the anticipated reduction in ambient $PM_{2.5}$, there were some surprising findings in this study. The reduction in woodsmoke-related $PM_{2.5}$ was accompanied by unexpected reductions in $PM_{2.5}$ from the other sources, including secondary SO_4 (−23%), secondary NH_4NO_3 (−13%), and automobiles (−56%). Regarding the dramatic reduction in automobile emissions, it should be noted that CMB-identified levels were only reduced from 2.1 to 0.9 $\mu g/m^3$. Automobiles are considered a small $PM_{2.5}$ source in the Libby airshed. Elemental potassium concentrations were not significantly different following the changeout, whereas the potassium cation was almost 24% higher in the post-changeout winter period ($P = 0.057$). A reduction in potassium across the two winter periods might have been expected because potassium has often been used as an indicator of woodsmoke. However, potassium has also been reported to have questionable

utility as a woodsmoke marker because it has a relatively low (and highly variable) emission factor.[40] In addition, it is also present in suspended soil particulate.[41] Khalil and Rasmussen[40] reported a 63-fold increase in the emission factor for potassium from "hot" fires relative to "cool" fires. The current results are not conclusive but may suggest a similar change in the chemistry of the $PM_{2.5}$ emissions with the introduction of the new EPA-certified stoves, which are expected to have a higher combustion temperature. These findings are consistent with some of the authors' other ambient studies in Libby in which increases in resin acids (dehydroabietic and abietic acids) have been measured in the ambient air following the Libby woodstove changeout. It was expected that these resin acids (chemical markers of woodsmoke from softwood combustion) would mimic the reductions in the observed values of levoglucosan.[38]

CONCLUSIONS

When comparing the $PM_{2.5}$ mass results of 2003–2004 with post-changeout concentrations of 2007–2008, there was a 20% reduction when using the FRM sampler measurements (28% when comparing the speciated sampler values). Results from the CMB source apportionment studies showed that there was a 28% reduction in the woodsmoke source contributions to the wintertime $PM_{2.5}$. Even after the significant reductions in biomass smoke-related $PM_{2.5}$, residential woodstoves continue to be the largest source of $PM_{2.5}$ in Libby. The results of these studies also show that the chemistry of the emitted $PM_{2.5}$ has been altered.

Although it is likely that Libby will meet the annual $PM_{2.5}$ NAAQS, the community may still have issues because the daily standard was revised from 65 to 35 $\mu g/m^3$ in 2007. This is related to the meteorological and topographical conditions experienced in Libby (severe temperature inversions in a small valley community) in combination with the existing emissions from sources within the valley. Given that most stoves are now modern and certified to emit low levels of particulate matter, any further improvements in Libby air quality will likely have to come from elimination of some woodstoves in favor of other sources of heat. Regardless, the results from this program show that woodstove changeouts can be an effective tool in reducing ambient levels of $PM_{2.5}$ in woodstove smoke-impacted airsheds.

REFERENCES
1. Sexton, K.; Spengler, J.D.; Treitman, R.D. Winter Air Quality in a Wood-Burning Community: a Case Study in Waterbury, Vermont; *Atmos. Environ.* **1984**, *18*, 1357-1370.

2. Fairley, D. The Relationship of Daily Mortality to Suspended Particulates in Santa Clara County, 1980–1986; *Environ. Health Perspect.* **1990**, *89,* 159-168.
3. McDonald, J.D.; Zielinska, B.; Fujita, E.M.; Sagebiel, J.C.; Chow, J.C.; Watson, J.G. Fine Particle and Gaseous Emission Rates from Residential Wood Combustion; *Environ. Sci. Technol.* **2000**, *34,* 2080-2091.
4. Schauer, J.J.; Cass, G.R. Source Apportionment of Wintertime Gas-Phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers; *Environ. Sci. Technol.* **2000**, *34,* 1821-1832.
5. Fine, P.M.; Cass, G.R.; Simoneit, B.R.T. Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Northeastern United States; *Environ. Sci. Technol.* **2001**, *35,* 2665-2675.
6. Polissar, A.V. Hopke. P.K.; Poirot, R.L. Atmospheric Aerosol over Vermont: Chemical Composition and Sources; *Environ. Sci. Technol.* **2001**, *35,* 4604-4621.
7. Maykut, N.N.; Lewtas, J.; Kim, E.; Larson, T.V. Source Apportionment of PM$_{2.5}$ at an Urban IMPROVE Site in Seattle, Washington; *Environ. Sci. Technol.* **2003**, *37,* 5135-5142.
8. Larson, T.; Gould, T.; Simpson, C.; Liu, L.J.; Claiborn, C.; Lewtas, J. Source Apportionment of Indoor, Outdoor, and Personal PM$_{2.5}$ in Seattle, Washington, Using Positive Matrix Factorization; *J. Air & Waste Manage. Assoc.* **2004**, *54,* 1175-1187.
9. Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Chen, L.W.A.; Zielinska, B.; Mazzoleni, L.R.; Magliano, K.L. Evaluation of Organic Markers for Chemical Mass Balance Source Apportionment at the Fresno Supersite; *Atmos. Chem. Phys.* **2007**, *7,* 1741-1754.
10. Su, J.G.; Larson, T.; Baribeau, A.M.; Brauer, M; Rensing, M.; Buzzelli, M. Spatial Modeling for Air Pollution Monitoring Network Design: Example of Residential Woodsmoke; *J. Air & Waste Manage. Assoc.* **2007**, *57,* 893-900; doi: 10.3155/1047-3289.57.8.893.
11. Luhar, A.K.; Galbally, I.E.; Keywood, M. Modeling PM$_{10}$ Concentrations and Carrying Capacity Associated with Woodheater Emissions in Launceston, Tasmania; *Atmos. Environ.* **2006**, *40,* 5543-5557.
12. Puxbaum, H.; Caseiro, A.; Sanchez-Ochoa, A.; Kasper-Giebl, A.; Claeys, M.; Gelencser, A.; Legrand, M.; Preunkert, S.; Pio, C. Levoglucosan Levels at Background Sites in Europe for Assessing the Impact of Biomass Combustion on the European Aerosol Background; *J. Geophys. Res.* **2007**, 112, D23S05; doi: 10.1029/2006JD008114.
13. Szidat, S.; Prevot, A.S.H.; Sandradewi, J.; Alfarra, M.R.; Synal, H.-A.; Wacker, L.; Baltensperger, U. Dominant Impact of Residential Wood Burning on Particulate Matter in Alpine Valleys during Winter; *Geophys. Res. Lett.* **2007**, *34,* L05820; doi: 10.1029/2006GL028325.25.
14. Alfarra, M.R.; Prevot, A.S.H.; Szidat, S.; Sandradewi, J.; Weimer, S.; Lanz, V.A.; Schreiber, D.; Mohr, M.; Baltensperger, U. Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions; *Environ. Sci. Technol.* **2007**, *41,* 5770-5777.
15. Lanz, V.A.; Alfarra, M.R.; Baltensperger, U.; Buchmann, B.; Hueglin, C.; Szidat, S.; Wehrli, M.N.; Wacker, L.; Weimer, S.; Caseiro, A.; Puxbaum, H.; Prevot, A.S.H. Source Attribution of Submicron Organic Aerosols during Wintertime Inversions by Advanced Factor Analysis of Aerosol Mass Spectra; *Environ. Sci. Technol.* **2008**, *42,* 214-220.
16. Olivares G.; Strom, J.; Johansson, C.; Gidhagen, L. Estimates of Black Carbon and Size-Resolved Particle Number Emission Factors from Residential Wood Burning Based on Ambient Monitoring and Model Simulations; *J. Air & Waste Manage. Assoc.* **2008**, *58,* 838-848; doi: 10.3155/1047-3289.58..6.838.
17. Ward, T.J.; Smith, G.C. The 2000/2001 Missoula Valley PM$_{2.5}$ Chemical Mass Balance Study, Including the 2000 Wildfire Season-Seasonal Source Apportionment; *Atmos. Environ.* **2004**, *39,* 709-717.
18. Ward, T.J.; Rinehart, L.R.; Lange, T. The 2003/2004 Libby, Montana PM$_{2.5}$ Source Apportionment Research Study; *Aerosol Sci. Technol.* **2006**, *40,* 166-177.
19. Ward, T.J.; Lange, T. The Impact of Wood Smoke on Ambient PM$_{2.5}$ in Northern Rocky Mountain Valley Communities; *Environ. Pollut.* **2010**, *158,* 723-729.
20. *Recommendations to the Clean Air Act Advisory Committee*; Air Quality Management Work Group: Washington, DC, 2005.
21. Houck, J.E.; Broderick, D.R.; Keithley, C. All Eyes on Libby; *Hearth and Home* **2005**, *February,* 68-86.
22. Carlin, J. *Libby, Montana PM$_{2.5}$ Annual Standard: 2005 PM$_{2.5}$ Emission Inventory*; Montana Department of Environmental Quality: Helena, MT, 2008.
23. Eagle, B.; Houck, J.E. *Phase I of the Libby, Montana Woodstove Changeout Program*; OMNI Environmental Services: Portland, OR, 2007.
24. Eagle, B.; Houck, J.E. *Phase II of the Libby, Montana Woodstove Change-out Program*; OMNI Environmental Services: Portland, OR, 2007.
25. *PM$_{2.5}$ Monitoring Information. Speciation Laboratory Standard Operating Procedures for Gravimetric, X-Ray Fluorescence, Ion, and Organic Carbon/Elemental Carbon Analyses*; U.S. Environmental Protection Agency; Technology Transfer Network Ambient Monitoring Technology Information Center: Research Triangle Park, NC, 2005; available at *http://www.epa.gov/ttn/amtic/specsop.html* (accessed 2010).
26. Friedlander, S.K. Chemical Element Balances and Identification of Air Pollution Sources; *Environ. Sci. Technol.* **1973**, *7,* 235-240.
27. Cooper, J.A.; Watson, J.G. Receptor Oriented Methods of Air Particulate Source Apportionment; *J. Air Pollut. Control Assoc.* **1980**, *30,* 1116-1125.
28. Gordon, G.E. Receptor Models; *Environ. Sci. Technol.* **1980**, *14,* 792-800.
29. Gordon, G.E. Receptor Models; *Environ. Sci. Technol.* **1988**, *22,* 1132-1142.
30. Watson, J.G. Overview of Receptor Model Principles; *J. Air Pollut. Control Assoc.* **1984**, *34,* 619-623.
31. Watson, J.G.; Cooper, J.A.; Huntzicker, J.J. The Effective Variance Weighting for Least Squares Calculations Applied to the Mass Balance Receptor Model; *Atmos. Environ.* **1984**, *18,* 1347-1355.
32. Hidy, G.M.; Venkataraman, C. The Chemical Mass Balance Method for Estimating Atmospheric Particle Sources in Southern California; *Chem. Eng. Comm.* **1996**, *151,* 187-209.
33. *SPECIATE 3.2: U.S. Environmental Protection Agency (EPA)'s Repository of Total Organic Compound (TOC) and Particulate Matter (PM) Speciated Profiles for a Variety of Sources for Use in Source Apportionment Studies*; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 2002; available at *http://www.epa.gov/ttn/chief/software/speciate/index* (accessed 2010).
34. Carlson, J. PM$_{10}$ *Chemical Mass Balance Study for Missoula, Montana*; Missoula City–County Health Department: Missoula, MT, 1990.
35. Schmidt, B. *Chemical Mass Balance Source Apportionment of Missoula, Montana 1995/1996 Winter Suspended Particulate Matter*; Missoula City–County Health Department: Missoula, MT, 1996.
36. Watson, J.G. *Protocol for Applying and Validating the CMB Model for PM$_{2.5}$ and Volatile Organic Compound*; EPA-451/R-04-001; Prepared by Desert Research Institute, Reno, NV, for the U.S. Environmental Protection Agency: Research Triangle Park, NC, 2004.
37. Ward, T.J.; Palmer, C.P.; Houck, J.E.; Navidi, W.C.; Geinitz, S.; Noonan, C.W. A Community Woodstove Changeout and Impact on Ambient Concentrations of Polycyclic Aromatic Hydrocarbons; *Environ. Sci. Technol.* **2009**, *43,* 5345-5350.
38. Bergauff, M.A.; Ward, T.J.; Noonan, C.W.; Palmer, C.P. The Effect of a Woodstove Changeout on Ambient Levels of PM$_{2.5}$ and Chemical Tracers for Woodsmoke in Libby, Montana; *Atmos. Environ.* **2009**, *43,* 2938-2943.
39. Ward, T.J.; Palmer, C.; Bergauff, M.; Hooper, K.; Noonan, C. Results of a Residential Indoor PM$_{2.5}$ Sampling Program before and after a Woodstove Changeout; *Indoor Air* **2008**, *18,* 408-415.
40. Khalil, M.A.K.; Rasmussen, R.A. Tracers of Wood Smoke; *Atmos. Environ.* **2003**, *37,* 1211-1222.
41. Calloway, C.P.; Li, S.; Buchanan, J.W.; Stevens, R.K. A Refinement of the Potassium Tracer Method for Residential Wood Smoke; *Atmos. Environ.* **1989**, *23,* 67-69.

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