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Community Woodstove Changeout and Impact on Ambient Concentrations of Polycyclic Aromatic Hydrocarbons and Phenolics

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A large woodstove changeout program was carried out in Libby, Montana, with the goal of reducing ambient levels of PM_{2.5}. This provided researchers the opportunity to measure ambient concentrations of phenolic and polycyclic aromatic hydrocarbons (PAHs) before, during, and after the changeout of nearly 1200 stoves to evaluate the effectiveness of the intervention. Starting in the heating season of 2004/2005 and ending in the heating season of 2007/2008, 19 compounds were measured every three days using a high-volume polyurethane foam (PUF) sampler followed by gas chromatography and mass spectrometry analysis. Some of the organic species with the highest measured concentrations were also signature chemical markers for wood combustion. When comparing the measurements conducted during the heating season of 2004/2005 (prechangeout) to those of the heating season of 2007/2008 (postchangeout), there was a 64% average reduction in the measured concentrations of phenolics and PAHs, while the PM_{2.5} mass dropped by only 20% over the same time period. The results of this four year sampling program suggest that the Libby woodstove changeout program was successful in reducing overall concentrations of the measured phenolic and PAH compounds.

Introduction

Libby is a small community located in a high mountain valley (elevation of 628 m) in northwestern Montana. The population of Libby is ~2700, with nearly 12000 in the Greater Libby Valley. There is currently no natural gas line serving the city. Therefore, home heating is accomplished using electric,

propane, oil, or wood-burning heating devices. It is estimated that there are approximately 1500 homes in Libby and the surrounding valley that use wood as a primary or secondary source of heat (1).

The Libby Valley frequently experiences temperature inversions throughout the heating season months that have historically contributed to elevated levels of ambient PM_{2.5} (fine particulate matter). Before the woodstove changeout, the heating season PM_{2.5} concentrations were so high that Libby exceeded the annual PM_{2.5} National Ambient Air Quality Standard (NAAQS) of 15 μg/m³, resulting in Libby being designated as a nonattainment area for PM_{2.5}. Prior to the revised daily NAAQS in 2007, Libby was the only PM_{2.5} nonattainment area west of the Mississippi River and outside of southern California.

During the heating season of 2003/2004, a source apportionment program was conducted in Libby to identify the sources of PM_{2.5}. During this program, PM_{2.5} mass concentrations averaged 28.2 μg/m³. Results of chemical mass balance (CMB) modeling identified residential wood combustion as the major source of PM_{2.5} during the heating season (2). There are no significant industrial sources in the Libby airshed, and although various area sources and background contributions to airshed PM_{2.5} levels have been quantified, individually they are small.

In response to these findings, a large woodstove changeout program was implemented in 2005, with funding provided by the U.S. Environmental Protection Agency (EPA), the Hearth, Patio, and Barbeque Association (HPBA), and the Montana Department of Environmental Quality (DEQ). In this context the term “changeout” refers to the removal of older, high-emitting woodstoves and replacement with EPA-certified woodstoves that meet the emission standards of 7.5 g/h of PM for conventional models. The changeout also includes modification or refitting of existing certified stoves that were not operating efficiently as well as the surrender or decommissioning of older woodstoves in favor of other nonbiomass heating sources. Before the start of the program, there were approximately 1300 uncertified “dirty” woodstoves registered in Libby and another 100 wood burning furnaces or boilers. At the conclusion of the woodstove changeout program in 2007, nearly 1200 old woodstoves were changed out, modified, or surrendered.

Concentrations of phenolic and polycyclic aromatic hydrocarbons (PAHs) were measured to track the ambient air quality during the changeout and to evaluate the effectiveness of the woodstove changeout at the conclusion of the program. PAHs are an important subgroup of organic compounds because of their potential carcinogenic properties (3–5). Phenolic compounds and PAHs measured in this study are pyrolysis and pyrosynthesis products primarily of the lignin found in wood fuel. Phenolics are an expected byproduct of biomass combustion because the lignin content of wood is characterized by phenolic units joined by propane linkers (6).

In controlled studies, the pyrolysis of lignin and representative compounds have shown that yields of PAHs generally increase with pyrolysis temperature and residence time, indicating a kinetically controlled pyrosynthesis pathway (7–9). Additionally, the relative amounts of larger PAHs with greater than three rings has been shown to increase with pyrolysis temperature (8–10). PAH profiles, in which individual PAH concentrations are normalized either to the concentration of a selected PAH or to the sum of all PAHs, have often been shown to vary significantly with the source (4, 11–13). Such profiles are known to be affected by aging

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processes because the reactivity of individual PAHs varies significantly (12, 14–18) and by combustion or pyrolysis conditions (7–9, 11).

The emission factors (mass of emitted compound per kilogram of wood fuel) of SVOCs (semivolatile organic compounds, including phenols and PAHs) and PM (particulate matter) for noncatalytic certified stoves have been compared to older wood stove models. Comparisons of older model woodstoves to certified noncatalytic models showed a 33–50% reduction in the average particle emission rates and smaller fractions of PM_{2.5} and PM₁₀ (19, 20). Airflow setting, however, can have a more significant effect on particulate matter emissions than stove design (21). The EPA reported in 1996 that certified stoves had lower emission factors for nine of thirteen PAHs for which data was available, with the average reduction being 52% (19). Emission factors for phenanthrene (3 ring), benzo[*a*]pyrene (5 ring) and benzo[*g,h,i*]perylene (6 ring) increased, while that of anthracene (3 ring) remained unchanged. Two more recent studies of woodstove emissions reported that emission factors for semivolatiles were the same or higher with certified stoves (20, 21). These increased emission factors were explained by higher burn temperatures and longer residence times in the certified stoves (21).

The first “whole town” woodstove 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 air pollution during the subsequent heating season (22). It has also been demonstrated that changing out an old, polluting stove with a new EPA-certified one can have a dramatic impact on indoor air quality within the home (23). In a residential study conducted in Libby, indoor levels of PM_{2.5} were significantly reduced following the changeout of an old stove with an EPA-certified stove. In this work, we present the results of the ambient PAH sampling program conducted before, during, and following the Libby woodstove changeout program.

Experimental Section

The woodstove changeout in Libby was carried out in two phases. During phase I (June 2005 to June 2007), 260 uncertified woodstoves were replaced with certified cleaner burning woodstoves within the homes of low-income families in the Libby area. Pellet and gas installations were not an option during phase I. From January 2006 through June 2007, phase II was targeted toward changing out the remaining ~900 uncertified wood-burning appliances in Libby with newer, low emission, and more efficient wood, pellet, propane, oil, or electric home-heating devices. Phase II also included a stove rebuild or catalytic unit replacement program that rebuilt or refit up to 100 existing certified stoves that were still usable but not properly operating because of their condition. Low-income eligibility was no longer the driving force of changeouts in phase II as compared to phase I (1, 24).

During both phases of the program, the majority of the residents changed out their old woodstoves with new, conventional, EPA-certified woodstoves that met the 1988 EPA certification emissions standards of less than 7.5 g/h of particulate matter 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, and furnaces, wood inserts, pellet stoves, pellet inserts, pellet furnaces, oil stoves and furnaces, electric heaters, and wood furnaces. The amount of cordwood burned in Libby per appliance prior to

the changeout has been estimated at between 3.5 and 4.8 cords per season, with the species of trees used for fuel including western larch, Douglas fir, and Ponderosa pine (25).

Using samplers sited on the roof of the Lincoln County Environmental Health Building in downtown Libby, Lincoln County personnel collected ambient air samples every three days (24 h, midnight to midnight) from November through the end of February for each of the four heating seasons (2004/2005, 2005/2006, 2006/2007, and 2007/2008) following the fixed monitoring schedule of the EPA. Samples were collected using a high-volume PUF sampler per EPA Compendium Method TO-13A (26).

The Andersen Model GPS1-1 high-volume PUF sampler consisted of a 102 mm circular quartz glass filter that collected total suspended particulates (TSPs), followed by a 60 mm ID × 125 mm borosilicate glass sorbent cartridge containing a PUF sorbent that collected vapor-phase SVOCs that either passed through the filter during sampling or were stripped off of the particles entrapped on the filter during sampling. In addition to the PUF sampler, the Montana DEQ and Lincoln County personnel operate other air samplers at the site, including Federal Reference Method (FRM) PM_{2.5} samplers (BGI PQ200s) that accurately measure PM_{2.5} mass concentrations every third day following the fixed monitoring schedule of the EPA. The PUF sampler and the FRM PM_{2.5} samplers ran on the same three day schedules throughout the four year heating season sampling programs.

The filter and PUF samples were analyzed for phenolics and PAHs per EPA Compendium Method TO-13A (26). In the first step of the procedure, the filter and PUF cartridge were extracted together in 700 mL of 10% diethyl ether in a hexane solution. The Soxhlet apparatus refluxed overnight for 18 h at a rate of at least three cycles per hour. A Kuderna–Danish (K-D) concentrator was then used to evaporate the extract to an approximate volume of 5 mL before nitrogen blowdown to 1 mL. Extracts were analyzed using a Hewlett Packard 6890 series GC with a 5973 mass selective detector (GC/MS). As part of the analysis, a suite of 19 SVOCs (including phenolic compounds and PAHs) were quantified using a 0.32 mm ID × 30.0 m Restek XTI-5 column (film thickness of 1.0 μm). The MSD operated using the full scan mode, and analytes were identified on the basis of the selected ion(s) characteristics for each analyte.

Quality assurance/quality control (QA/QC) for the PUF sampler included a multipoint calibration that was conducted prior to the start of the sampling programs (and after motor replacements) and single-point flow audits that were conducted during each of the monthly site visits. Field blanks (high-volume quartz filters and PUF cartridges) were collected to provide an estimate of the total measurement system contamination due to field activities. For the filter/PUF analyses, quality control throughout the program included the use of field and laboratory surrogates and laboratory control spikes. The field surrogates included D₁₀-fluoranthene and D₁₂-benzo[*a*]pyrene, while the lab surrogates included D₁₀-fluorene and D₁₀-pyrene. One microgram of each of the field surrogate compounds was spiked into the PUF cartridge before the sample episode, while 1 μg of each of the laboratory surrogate compounds was spiked onto the PUF cartridge just before extraction. QA/QC measures for the GC/MS included the analysis of decafluorotriphenylphosphine (DFTPP) at the start of each day for the SVOC analyses to ensure instrument stability and sensitivity. Mid-range standards were also run during each day of sample analyses to verify initial calibrations (continuing calibrations). Internal standards (D₈-naphthalene, D₁₀-acenaphthene, D₁₀-phenanthrene, and D₁₂-chrysene) were spiked into calibration standards to quantify analyte concentrations.

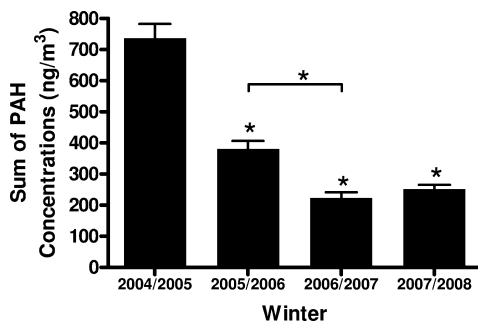


FIGURE 1. Crude mean winter sum of Libby ambient PAH and phenolic concentrations over the four year sampling program. * represents $p < 0.05$ compared to baseline year or as indicated.

For data analysis, general linearized models were constructed using R v2.8. Several meteorological and air quality factors vary with time and can be associated with release, formation, or environmental persistence of volatile chemicals, which could account for the observed changes in SVOCs. For each compound, we computed adjusted mean levels for each of the four years as follows to account for these time-varying factors. We considered $PM_{2.5}$, temperature, relative humidity, and precipitation on the same day and lagged one day as potential adjustment factors. We computed the correlation of each of these variables with concentration for each year separately. Variables that were significant at the 0.15 level for two or more of the four years were used for adjustment. To compute adjusted yearly means, we fit a separate linear model by ordinary least-squares for each year, regressing concentration against the adjustment factors selected for that compound. The adjusted mean concentration for a given year was computed by substituting the mean levels, computed over all four years, of the selected adjustment factors. We constructed 95% confidence intervals using the standard method for constructing a confidence interval for the mean response in a linear model (27). To check for autocorrelation, we computed the Durbin–Watson statistic for each compound for each year.

Results and Discussion

The changeout program was initiated following the baseline year (2004/2005), but only 9.3% of the targeted 1175 woodstoves had been removed, reconditioned, or replaced by the beginning of the 2005/2006 PAH sampling program. By the start of the 2006/2007 heating season, the woodstove changeout program was 58.7% complete. By the start of the final 2007/2008 heating season, the woodstove changeout program was 96.2% complete.

Phenolics and PAHs. Out of the 162 scheduled sampling events over the four heating season period, 160 were successfully collected and analyzed. For each 24 h sampling event, an average of 356.3 m³ of air was collected following EPA's Compendium Method TO-13A (26).

PAH and phenolic concentrations measured in year 1 (2004/2005) of the program reflect prechangeout concentrations and are the highest when compared to those of the following three heating seasons. When comparing the concentrations of the measured compounds before and following the changeout, there is a dramatic reduction (Figure 1).

Table 1 presents the average SVOC (phenolics and PAHs) concentrations (and standard deviations) measured during each of the heating season programs. Results are not blank corrected. Throughout the program, the compounds with the highest measured concentrations were 2-methylphenol (*p*-cresol), phenol, 2,4-dimethylphenol, 4-methylphenol (*p*-cresol), and phenanthrene. Comparing the postchangeout

measurements (2007/2008) with the prechangeout measurements (2004/2005), there was a 50–83% reduction in SVOC concentrations. These crude reductions did not change appreciably after adjusting for $PM_{2.5}$ and meteorological data. The only compounds and years that showed substantial positive autocorrelation (Durbin–Watson statistic < 1) were phenanthrene (year 1), fluoranthene (years 1 and 4), and pyrene (years 1 and 4). As a result, the standard errors and confidence intervals for these compounds for these years may be somewhat underestimated.

Figure 1 also shows that the greatest reduction occurred between the heating seasons of 2004/2005 and 2005/2006 or the first two heating seasons of the sampling program. The changeout program was initiated following the baseline year (2004/2005), yet only 9.3% of the targeted 1175 woodstoves had been removed, reconditioned, or replaced by an EPA-certified woodstove by the beginning of the 2005/2006 (year 2) PAH sampling program. By the start of the 2006/2007 PAH sampling, the woodstove changeout program was 58.7% complete. This dramatic drop of PAHs over the first two years of the program could be the result of the phase I program targeting the most polluting of the non-EPA-certified woodstoves.

There was also a small (nonsignificant) increase in the overall summed PAH and phenolic concentrations between years 3 (2006/2007) and 4 (2007/2008) of the program. By the start of the 2006/2007 (year 3) PAH sampling, the woodstove changeout program was 58.7% complete, with 96.2% program completion by the start of the final 2007/2008 (year 4) PAH sampling program. In addition, normalization of the PAH concentrations to the concentration of naphthalene shows a nearly identical profile in comparing the 2004/2005 and 2007/2008 heating seasons (Figure 2). The profile is essentially the same regardless of which PAH is used for normalization or if the individual PAHs are normalized to the sum of all PAHs measured. The similarity in the profile implies that the PAHs measured during these two seasons are from the same or similar source, are produced under similar pyrolysis or combustion conditions, and are aged to a similar extent.

Ambient $PM_{2.5}$. Table 2 presents the $PM_{2.5}$ mass concentration averages measured during the heating seasons of 2004/2005, 2005/2006, 2006/2007, and 2007/2008. Also included in Table 2 are those days which exceeded the 24 h NAAQS of 35 $\mu\text{g}/\text{m}^3$. Results are not blank corrected.

There was a 20% reduction in ambient $PM_{2.5}$ mass when comparing the prechangeout heating season (2004/2005) with the postchangeout heating season (2007/2008) (Figure 3). Average ambient $PM_{2.5}$ concentrations ($\mu\text{g}/\text{m}^3$) in year 3 (2006/2007) were lower than those of the 2003/2004 baseline year [mean diff. (95% CI) = -4.9 (-1.2 to -8.7)], but there was no further significant reduction between 2006/2007 and 2007/2008. Potentially more significant from a regulatory point of view is that there was also a reduction in the number of 24 h NAAQS exceedances when comparing those of the baseline heating season 2004/2005 with those of the last year of the program (heating season 2007/2008). In the heating season of 2004/2005, there were six days in which the $PM_{2.5}$ mass exceeded 35 $\mu\text{g}/\text{m}^3$ (note that the 24 h $PM_{2.5}$ NAAQS was 65 $\mu\text{g}/\text{m}^3$ in 2004/2005). During the heating season of 2007/2008 (November 2, 2007 through March 1, 2008), the daily NAAQS was exceeded on only one occasion (January 4, 2008, 42.3 $\mu\text{g}/\text{m}^3$).

QA/QC. Throughout the four year sampling program, each of the single-point flow audits were $\pm 10\%$ of the desired flow rate per EPA specifications. All DFTPP runs passed laboratory quality criteria before samples were analyzed for that day, and daily GC/MS continuing calibration results were generally well within the desired range of $\pm 30\%$ for each of the days that samples were analyzed throughout each of the four years. For the field blanks, phenol, naphthalene, phenanthrene,

TABLE 1. Unadjusted Phenolic and PAH Average Heating Season Concentrations ± Standard Deviations and Adjusted Percent Reductions

SVOC compound	2004/2005 concentrations (ng/m ³)	2005/2006 concentrations (ng/m ³)	2006/2007 concentrations (ng/m ³)	2007/2008 concentrations (ng/m ³)	crude percent reduction ^a	adjusted percent reduction (95% CI) ^{a,b}
phenol	94.4 ± 52.6	69.8 ± 41.6	36.6 ± 27.6	46.8 ± 24.5	-50	-56.3(-36.7,-75.9)
2-methylphenol (<i>o</i> -cresol)	72.1 ± 37.4	38.8 ± 18.1	21.9 ± 14.2	25.4 ± 10.5	-65	-69.4(-53.8,-85.0)
4-methylphenol (<i>p</i> -cresol)	148.4 ± 72.0	83.4 ± 38.0	44.4 ± 25.2	55.3 ± 20.9	-63	-63.5(-49.0,-78.1)
2,4-dimethylphenol	76.5 ± 39.1	43.5 ± 18.0	18.7 ± 10.5	21.3 ± 9.0	-72	-70.0(-53.5,-86.5)
naphthalene	27.8 ± 22.7	9.0 ± 6.0	10.8 ± 7.7	8.7 ± 5.7	-69	-71.0(-55.9,-86.1)
2-methylnaphthalene	30.5 ± 21.3	8.2 ± 4.0	9.2 ± 5.8	9.7 ± 5.5	-68	-67.9(-53.6,-82.1)
acenaphthylene	46.3 ± 33.1	9.7 ± 4.9	7.7 ± 4.3	7.9 ± 3.2	-83	-79.7(-60.2,-99.1)
acenaphthene	4.8 ± 2.7	2.4 ± 0.9	2.1 ± 1.1	2.2 ± 0.9	-54	-48.8(-36.1,-61.6)
dibenzofuran	34.0 ± 15.8	17.3 ± 7.0	11.8 ± 5.3	12.4 ± 4.3	-64	-57.2(-45.9,-68.5)
fluorene	24.8 ± 12.6	11.2 ± 4.4	8.3 ± 3.4	7.7 ± 2.6	-69	-62.7(-51.5,-73.8)
phenanthrene	75.8 ± 44.0	38.3 ± 16.2	26.5 ± 11.7	24.4 ± 8.0	-68	-62.3(-48.2,-76.5)
anthracene	12.1 ± 7.0	4.6 ± 2.0	3.7 ± 1.5	2.9 ± 0.9	-76	-69.7(-55.8,-83.5)
fluoranthene	27.8 ± 14.7	11.5 ± 4.8	7.9 ± 3.6	8.1 ± 2.8	-71	-66.8(-50.3,-83.2)
pyrene	26.0 ± 13.9	9.9 ± 4.3	6.6 ± 3.1	7.0 ± 2.8	-73	-68.0(-54.1,-81.8)
benzo[<i>a</i>]anthracene	12.1 ± 7.2	5.1 ± 1.7	2.1 ± 1.0	3.8 ± 1.6	-69	-61.9(-49.0,-74.8)
chrysene	10.7 ± 5.8	6.1 ± 2.3	2.2 ± 0.6	2.5 ± 1.2	-76	-72.1(-64.5,-79.6)
benzo[<i>b</i>]fluoranthene	6.2 ± 3.5	6.1 ± 1.9	1.6 ± 0.3	3.3 ± 1.0	-47	-35.0(-22.7,-47.2)
benzo[<i>k</i>]fluoranthene	6.7 ± 4.2	6.4 ± 2.2	1.7 ± 0.4	1.9 ± 1.1	-72	-63.0(-50.5,-75.5)
benzo[<i>a</i>]pyrene ^c	6.3 ± 4.4	not analyzed	1.0 ± 1.2	not detected	-	-

^a Values comparing year 1 (2004/2005) to year 4 (2007/2008). ^b Values are based on least-squares means adjusted for PM_{2.5}, temperature, relative humidity, precipitation, and wind speed, as appropriate. ^c Benzo[*a*]pyrene was not analyzed and/or detected from the 2005/2006 and 2007/2008 samples due to poor analytical sensitivity.

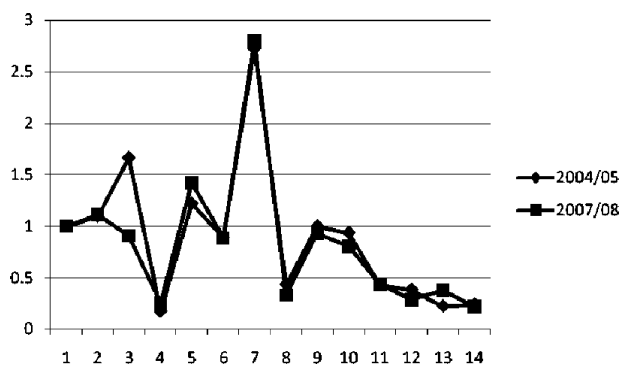


FIGURE 2. Measured levels of PAHs normalized to naphthalene, in order of increasing number of rings: (1) naphthalene, (2) 2-methyl naphthalene, (3) acenaphthylene, (4) acenaphthene, (5) dibenzofuran, (6) fluorene, (7) phenanthrene, (8) anthracene, (9) fluoranthene, (10) pyrene, (11) benzo[*a*]anthracene, (12) chrysene, (13) benzo[*b*]fluoranthene, and (14) benzo[*k*]fluoranthene.

anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene showed low but persistent levels throughout the program. For anthracene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene, low level artifact contamination could potentially bias the sample results because the detected levels of these compounds within the air samples were so low. However, it should be noted that the levels detected for these compounds (in the blanks and in the samples) were at the lower end of the instrument detection limits at the conclusion of the program. The concentrations of the other contaminants were insignificant when compared to the elevated sample concentrations. For the spikes, average recoveries throughout the four year program were generally within the established criteria (60–120%) for the majority of the analytes. Average recoveries for all of the surrogates (field and lab) throughout the program, with the exception of d₁₂-benzo[*a*]pyrene, were generally well within the 60–120% acceptable range.

Particulate and SVOC Emissions. The current study shows a significant reduction in SVOCs and PM_{2.5} as a result

TABLE 2. PM_{2.5} Mass Average Concentrations ± Standard Deviations

year (heating season)	average, standard deviation (μg/m ³)	PM _{2.5} NAAQS exceedances
2004/2005	27.0 ± 12.5	1/19/2005, (75.3 μg/m ³) 1/22/2005, (52.8 μg/m ³) 2/3/2005, (45.9 μg/m ³) 11/5/2005, (39.7 μg/m ³) 11/23/2004, (37.7 μg/m ³) 2/27/2005, (35.0 μg/m ³)
2005/2006	26.0 ± 9.9	11/3/2005, (51.1 μg/m ³) 12/24/2005, (47.4 μg/m ³) 1/14/2006, (43.9 μg/m ³) 1/17/2006, (40.5 μg/m ³)
2006/2007	22.0 ± 8.5	11/1/2006, (41.2 μg/m ³) 12/22/2006, (40.0 μg/m ³) 12/25/2006, (39.6 μg/m ³)
2007/2008	21.8 ± 4.9	11/4/2006, (36.2 μg/m ³) 1/4/2008, (42.3 μg/m ³)

of the woodstove changeout program. Our findings in the Libby ambient study show greater reductions in SVOC emissions than did studies that were conducted under controlled conditions (19–21). In the current study, wood-

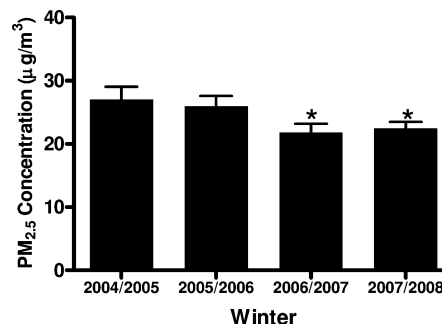


FIGURE 3. Mean winter ambient PM_{2.5} concentrations over the four year sampling program. * represents *p* < 0.05 compared to the baseline year.

stove replacement led to a 64% average reduction in ambient PAH concentrations. A similar percentage drop is observed for each of the PAHs leading to no substantial change in the PAH profile (Figure 2). The fact that the emission profile does not change indicates that the source, source combustion conditions, and age of the PAH emissions did not change substantially during the program.

PAHs versus PM_{2.5} Reductions. In this study, ambient PAH concentrations dropped by 64%, while the PM_{2.5} mass was lowered by only 20% over the same time period. In considering this difference, the half-lives of the PAHs versus the half-lives of the PM_{2.5} should be considered. Once emitted, PM_{2.5} can remain airborne for days and/or weeks under inversion conditions, whereas PAHs can break down fairly rapidly. Rapid photolytic degradation of PAHs on wood soot can occur with reaction half-times of less than an hour (14, 28). Other PAH degradation studies have shown a more rapid decay in a liquid mixture of methoxyphenols, an abundant class of compounds present in woodsmoke, than in hexadecane, which is representative of aliphatic hydrocarbons abundant in diesel soot and automobile exhaust (17). Particle-associated PAHs from woodsmoke have also been shown to decay rapidly in sunlight under some atmospheric conditions but are generally stable at night. Their reactivity is strongly influenced by solar radiation intensity, temperature, and atmospheric concentrations of water, ozone, and nitrogen oxides (15, 29). Even though there was a reduction in PM_{2.5} mass, the trapping of these PM_{2.5} emissions (versus the breakdown of the PAHs) in the airshed could have resulted in the differential impact of the changeout program on ambient concentrations of PM_{2.5} and PAHs.

There is also a possibility that the lower semivolatile emissions observed in this study are the result of reduced activity unrelated to woodstove changeout. The PAH emissions, in particular, are not specific to wood smoke. This explanation is very unlikely, however, because the economic and industrial activity in the area has not changed significantly, and there is no evidence that driving activity has changed during the study period. Finally, the similar PAH profile before and after the changeout implies a consistent emission source. On the basis of the earlier apportionment study, the most prevalent emission source at the beginning of this study was residential woodstoves.

Effectiveness of the Woodstove Changeout in Reducing Ambient Air Pollution. The results from this study provide strong empirical evidence that the replacement of uncertified conventional wood heaters with low-emitting heaters can provide substantial reductions in airshed PM_{2.5} and toxic air pollutant levels. These results are highly encouraging because they suggest that similar communities that rely heavily on woodstoves for residential heating can expect significant improvements in ambient air quality following the replacement of older woodstoves with more modern, certified appliances.

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