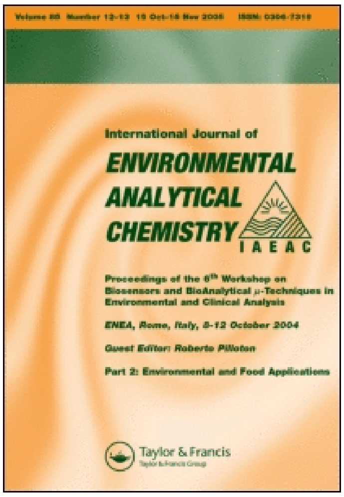

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Determination and evaluation of selected organic chemical tracers for wood smoke in airborne particulate matter

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$PM_{2.5}$ is released during combustion reactions and industrial processes. The chemical composition of PM can be a strong indicator of its origin, or source. A method was developed for the determination of selected chemical tracers for wood smoke in particulate matter using solvent extraction and GCMS analysis. The chosen tracers were levoglucosan, dehydroabietic acid, abietic acid, vanillin, acetovanillone, guaiacol, and 4-ethylguaiacol. Deuterated compounds of similar structure to the chosen tracers were employed as standards in the procedure to eliminate the possible effects of incomplete extraction from the filters and other fluctuations throughout the analysis period. The method had recoveries of 105 ± 7.7% for levoglucosan, 64 ± 3.5% for dehydroabietic acid, 60±3.6% for abietic acid, 98±2.2% for vanillin, 102 ± 3.8% for acetovanillone, 104 ± 4.9% for guaiacol and 116 ± 4.7% for 4-ethylguaiacol. The developed analytical method was applied to ambient particulate matter samples collected in Libby, MT. Libby has been designated as a non-attainment area for current USEPA $PM_{2.5}$ standards, and a recent study showed that 82% of the $PM_{2.5}$ in Libby resulted from residential wood smoke. The concentrations of levoglucosan, dehydroabietic acid, and abietic acid were found to be strongly correlated with total $PM_{2.5}$ levels in Libby, while the methoxyphenols did not show a correlation to $PM_{2.5}$ levels. Levoglucosan, dehydroabietic acid, and abietic acid were found to be suitable tracers for wood smoke in particulate matter.

Keywords: particulate matter; wood smoke; GCMS; chemical tracer; levoglucosan; resin acids; methoxyphenols

1. Introduction

The chemical composition of particulate matter, or PM, is a strong indicator of its origin, or source. Extensive characterization of the inorganic and organic composition permits apportionment of the total PM in an air shed to various sources. However, complete characterization of the chemical composition is expensive, and is not necessary to monitor specific intervention programmes. In such cases, it is more cost effective to determine the concentrations of selected specific chemical compounds that result from the specific source or sources of interest.

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In the current study, we report a method for the determination of selected organic markers of wood smoke in particulate matter. The specific markers were selected based on the results of a more complete analysis of particulate matter from a community where residential wood stoves are the dominant source of PM [1]. The new method is a combination and adaptation of previously reported methods, optimised for the selected set of markers [2–10]. We also apply this method to samples collected in a community with high exposure to residential wood smoke to evaluate the effectiveness of the selected analytes to act as markers for wood smoke in particulate matter.

Particulate matter with a diameter of 2.5 μm or less ($PM_{2.5}$) was chosen for this study because it can travel farther into the lungs than larger particles and is thus believed to have a greater effect on human health. $PM_{2.5}$ has been tied to increases in the amount of asthma attacks [11] and has been indicated to increase the number of hospitalizations for upper respiratory problems [12]. The United States Environmental Protection Agency's (USEPA) National Ambient Air Quality Standard allows for annual average $PM_{2.5}$ concentrations of up to 15 $\mu g\,m^{-3}$, or a daily concentration of up to 35 $\mu g\,m^{-3}$ [13]. For $PM_{2.5}$, an area is designated as nonattainment by the USEPA if it exceeds either the daily or annual standard, or if relevant information indicates that it contributes to violations in a nearby area.

Many rural communities have difficulty meeting these standards during the winter months due to $PM_{2.5}$ from residential wood stoves. One such $PM_{2.5}$ nonattainment area is the community of Libby, MT. Libby is a community of about 2,600 people located in a valley in north-western Montana. In 2003, there were approximately 1,300 registered wood stoves in Libby, with nearly 1,000 of those considered to be "dirty" wood stoves. The dirty stoves are older and complete combustion does not occur, releasing more particulates into the air. In Libby, the primary species of wood burned are softwoods, particularly Douglas fir and larch. Temperature inversions in the winter trap pollution in the valley, resulting in high levels of $PM_{2.5}$. $PM_{2.5}$ levels in Libby during the winter of 2003–04 [1] averaged 28.2 $\mu g\,m^{-3}$, with a high concentration of 40.9 $\mu g\,m^{-3}$. A Chemical Mass Balance model was used to determine that 82% of the ambient $PM_{2.5}$ levels were the result of residential wood burning emissions [1]. Particulate matter is routinely sampled and collected in many communities [14] so the most useful tracer for wood smoke would probably be found in the PM. Air sampling can also be done with polyurethane foam (PUF) to capture volatile compounds in the environment. Sampling with a PUF cartridge is more specialised than PM sampling, but it is not routinely conducted due to the higher cost, and the amount of time that is required.

Seven possible chemical markers for wood smoke exposure were selected from three different classes of compounds for continued monitoring of the $PM_{2.5}$ composition throughout a large-scale wood stove change-out programme (see Figure 1) in Libby. The chosen compounds are all known molecular markers for biomass combustion and were detected at significant levels in the preliminary study in Libby [1].

Levoglucosan is a pyrolysis product of cellulose and is generally one of the major organic components in ambient particulate matter from biomass combustion. It is frequently used as a tracer for biomass burning because it is produced at relatively high levels and is stable in the atmosphere [15]. The speciation study performed in Libby found that 13.9% of the total carbon in the particle phase is due to levoglucosan [1].

Resin acids occur naturally in wood, particularly in soft wood species such as pine, and can be released when the wood is burned or degraded. Resin acids have low solubility in water and can accumulate in tissues in fish or other organisms. They have been shown to

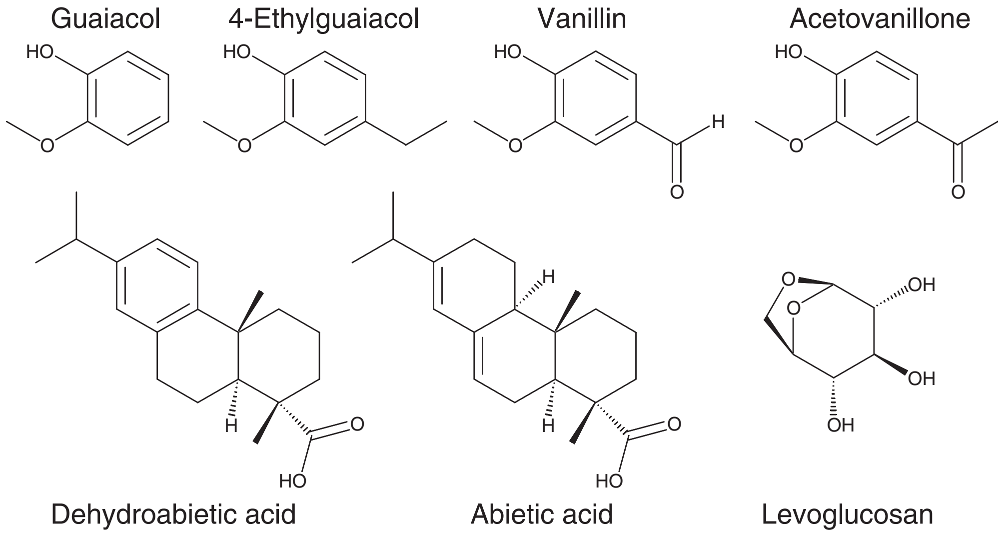

Figure 1. Structures of the selected chemical tracers for biomass burning.

have toxic effects on the liver and the potential to damage DNA [16]. The two resin acids selected to be monitored in this study are dehydroabietic acid and abietic acid. Dehydroabietic acid was the most prevalent resin acid measured during the comprehensive chemical speciation study performed on the Libby particulate matter during the 2003–04 study. Abietic acid can rapidly oxidise to dehydroabietic acid under atmospheric conditions and was found in significant levels in the initial study [1], so it was chosen to complement the dehydroabietic acid data.

Methoxyphenols result from pyrolysis of lignin, which is commonly found in cell walls of plants and is a waste product of the paper industry [17]. Some previous studies have suggested that various methoxyphenols in particulate matter can be used as tracers of wood smoke [8,17–19]. The type of wood burned (in particular, hardwood versus softwood) affects the ratio of guaiacols to syringols and other classes of methoxyphenols [17]. Unlike the other chosen compounds, the methoxyphenols are semi-volatile, so their presence will not be limited to the particulate phase [20]. The four methoxyphenols that were monitored in this study are vanillin, acetovanillone, guaiacol, and 4-ethylguaiacol. While all four of these methoxyphenols have been shown to exist predominantly in the vapour phase [21], the 2003–04 Libby study showed that they were all present in the particulate phase as well. In the original study, vanillin and acetovanillone were the two most abundant methoxyphenols measured [1].

Methods have been published for the analysis of multiple organic compounds in fine particulate matter [2–7,22] as well as for the specific determination of methoxyphenol [8]. and levoglucosan [9,10,15,23]. Resin acids such as dehydroabietic acid have been specifically investigated in forest fire smoke [24]. but not in residential wood smoke. Analysis of a large number of organic compounds can be costly and is not always necessary when investigating $PM_{2.5}$ from a single source. However, no method optimised for simultaneous determination of selected biomass burning tracers from multiple classes of compounds has been published. Our method combines analysis of residential wood smoke particulate for methoxyphenols and levoglucosan with a third group of wood smoke indicators, resin acids, for which no specific method has been optimised and reported. Conditions from the two published methods for methoxyphenols and levoglucosan have also been further optimised for faster analysis of particulates composed primarily of wood smoke. The method developed was applied to ambient samples collected in Libby, MT during the winter of 2004–05 to evaluate the method and to determine the usefulness of each of these compounds as a potential tracer for residential wood smoke in the particulate phase. Samples collected in Libby are a reasonable choice for this evaluation because the PM there is predominantly from wood smoke and the levels and environmental conditions vary significantly, giving a realistic situation [1].

2. Method

2.1 *Materials*

Vanillin 99%, acetovanillone 98%, guaiacol 99+%, 4-ethylguaiacol 98%, and levoglucosan 99+% were purchased from Acros Organics (Geel, Belgium). Abietic acid 90–95% was purchased from Alfa Aesar (Ward Hill, MA). Dehydroabietic acid (technical grade) was purchased from Pfaltz and Bauer Inc (Waterbury, CT). Ethyl acetate (reagent grade), triethylamine (reagent grade), and acetonitrile (HPLC grade) were purchased from Fisher Scientific (Hampton, NH). N-*O*-bis(trimethylsilyl)trifluoroacetamide (derivatization grade, 99+%), trimethylchlorosilane (97%), and trimethylsilylimidazole (derivatization grade) were purchased from Sigma (St. Louis, MO). All compounds were used as received except dehydroabietic acid, which was purified chromatographically in the lab using silica gel and mobile phase of dichloromethane (dehydroabietic acid purity estimated to be 85+% after purification).

2.2 *Standards*

Deuterated compounds of similar structure to the chosen tracers were employed as standards in the procedure to eliminate the possible effects of incomplete extraction from the filters and other variations throughout the analysis period. The chosen standards are D-vanillin as a standard for vanillin and acetovanillone, D-guaiacol as a standard for guaiacol and 4-ethylguaiacol, D-levoglucosan as a standard for levoglucosan, and D-stearic acid as a standard for abietic and dehydroabietic acid. The solutions containing D-stearic acid, D-vanillin, and D-guaiacol are prepared in ethyl acetate, while D-levoglucosan is prepared in acetonitrile. D-Vanillin (ring-5-D1) 98%, D-guaiacol (methoxy-D3) 98%, D-levoglucosan (D7) 98%, and D-stearic acid (D35) 98% were purchased from Cambridge Isotope Laboratories (Andover, MA).

2.3 *Sample collection*

Ambient particulate samples were collected every six days on the roof of the Lincoln County Annex in Libby, MT during the winter (November through February) of 2004–05. A BGI PQ200 $PM_{2.5}$ Federal Reference Method (FRM) $PM_{2.5}$ sampler was fitted with a quartz filter for each sample day to collect the ambient $PM_{2.5}$. Pre-fired 47-mm quartz filters were purchased from Chester LabNet (Tigard, OR), and delivered to Lincoln County personnel in a cooler. Clean quartz filters were stored in a refrigerator prior to sample collection. Following sample collection, the quartz filter samples were again stored in a refrigerator until analysed. Approximately 24 m^3 of air was sampled during each 24 hour episode. Four quartz filter field blanks were also collected throughout the programme to address artefact contamination. The average ambient temperature and average barometric pressure were also recorded with each 24-hour sampling period.

2.4 *Sample preparation*

Half of each 47 mm quartz filter sample was placed in a 30 mL vial and spiked with the 4 deuterated standards (D-vanillin, D-guaiacol, D-levoglucosan and D-stearic acid). The vials were capped and left at room temperature to allow the standards to be absorbed onto the filter. After half an hour, 20 mL of ethyl acetate with 3.6 mM triethylamine (TEA) was added and the samples were sonicated for half an hour to extract the desired compounds. After sonication, the filter was removed and the extract was filtered through a Whatman 0.45 µm nylon filter to remove particulates. The volume of the solvent was adjusted to 0.5 mL through evaporation under a stream of air in an oil bath at 45°C. The sample was then divided into two 250 µL portions. One portion was derivatized with 30 µL of a freshly prepared 2:3 mixture of acetic anhydride to triethylamine to be analysed for methoxyphenols. The other portion was evaporated to dryness under a stream of air at room temperature and then derivatized with 75 µL N-*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 10 µL trimethylchlorosilane (TMCS), and 10 µL trimethylsilylimidazole (TMSI) to be analysed for levoglucosan and the resin acids. Methoxyphenols were analysed as acetate derivatives, while levoglucosan and the resin acids were analysed as trimethylsilyl derivatives. Both portions were heated in an oil bath at 70°C for 1 hour to allow the derivatization to go to completion. Upon removal from the oil bath, the portion for methoxyphenols was transferred to a GC vial for analysis. The portion for levoglucosan and the resin acids was diluted to 250 µL with ethyl acetate containing 3.6 mM TEA and then was transferred to a GC vial for analysis.

2.5 *GC-MS analysis conditions*

Analysis was performed on an Agilent 6890N Gas Chromatograph with an Agilent 5973 Mass Spectrometer. An HP-5MS column ((5%-Phenyl)-methylpolysiloxane) was used with dimensions of 0.25 mm ID × 30 m length × 0.25 µm film thickness. A volume of 2 µL was injected for each analysis into a Split/Splitless FocusLiner$^{\text{TM}}$ for HP, single taper p/w quartz wool liner. Split injection was used to analyse for levoglucosan with a split ratio of 50:1 and splitless injection was used to analyse for the remaining compounds. The inlet temperature was set to 250°C and the auxiliary transfer line temperature was set at 280°C. The temperature programme was started at 40°C for 1.5 minutes, ramped at 30°C min^{-1} to 190°C, 20°C min^{-1} to 210°C, and then 50°C min^{-1} to a final temperature of 300°C, which was held for 1.5 minutes. The mass spectrometer was operated with a solvent delay of 4.00 minutes and the mass range from 40 to 450 was scanned. Single ion monitoring was also used during detection for guaiacol, D-guaiacol, and 4-ethylguaiacol with ions 124, 127 and 137. For all compounds, highly selective quantitation was performed using the signal for representative ions extracted from the total ion chromatogram (see Table 1 and Figure 2).

Table 1. Calibration range, quantification ions, and linearity of the calibration curves for the seven chosen tracers.

Compound	# of calibration points	Concentration range	R^2	Quantification ion
Levoglucosan	4	25–125 μg mL^{-1}	0.9925	217
D-Levoglucosan		80 μg mL^{-1}		220
Dehydroabietic acid	7	5–20 μg mL^{-1}	0.9820	239
Abietic acid	7	200–1000 ng mL^{-1}	0.9383	256
D-stearic acid		1 μg mL^{-1}		376
Vanillin	7	0.2–3 μg mL^{-1}	0.9908	151
Acetovanillone	7	0.2–3 μg mL^{-1}	0.9722	166
D-Vanillin		2 μg mL^{-1}		153
Guaiacol	4	2–20 ng mL^{-1}	0.9948	124
4-Ethylguaiacol	4	5–40 ng mL^{-1}	0.9969	137
D-Guaiacol		30 ng mL^{-1}		127

2.6 *Calibration and recovery*

Calibration standards were prepared containing variable concentrations of each selected tracer (see Table 1) and a fixed concentration of the corresponding deuterated internal standard. The fixed concentration of deuterated internal standard was selected to match the concentration expected from extraction of internal standard spiked on the filters, assuming 100% recovery. The standards were derivatized and analysed on the GCMS according to the determined conditions for each type of compound. The ratio of the peak area of the tracer to the peak area of the deuterated standard was found for each calibration standard. A calibration curve was prepared by plotting the ratio of the two peak areas versus the concentration of the tracer. Linearity was determined for each calibration curve, and all had R^2 values of at least 0.93 (see Table 1). The concentration of extracted analytes was determined by measuring the ratio of the peak area for the analyte to that of the corresponding deuterated standard, and reading the concentration from the appropriate calibration curve. Recoveries were calculated for filters spiked with the analytes at known amounts corresponding to typical levels seen in actual sample filters (see Table 2).

2.7 *$PM_{2.5}$ mass measurements*

$PM_{2.5}$ mass measurements were taken from the Montana Department of Environmental Quality compliance monitoring programme in Libby [25]. The net mass on a Teflon filter was determined gravimetrically by weighing the Teflon filter before and after sampling with a microbalance in a temperature and relative humidity controlled laboratory environment. $PM_{2.5}$ reference methods require that filters be equilibrated for 24 hours at a constant (±5%) relatively humidity between 30% and 40% and at a constant (±2°C) temperature between 20°C and 23°C to minimise particle volatilization and aerosol liquid water bias [25].

3. Results and discussion

3.1 *Method development and optimisation*

Various solvent systems have been reported in the literature for the extraction of organic compounds from particulate matter, including mixtures of ethyl acetate/triethyl

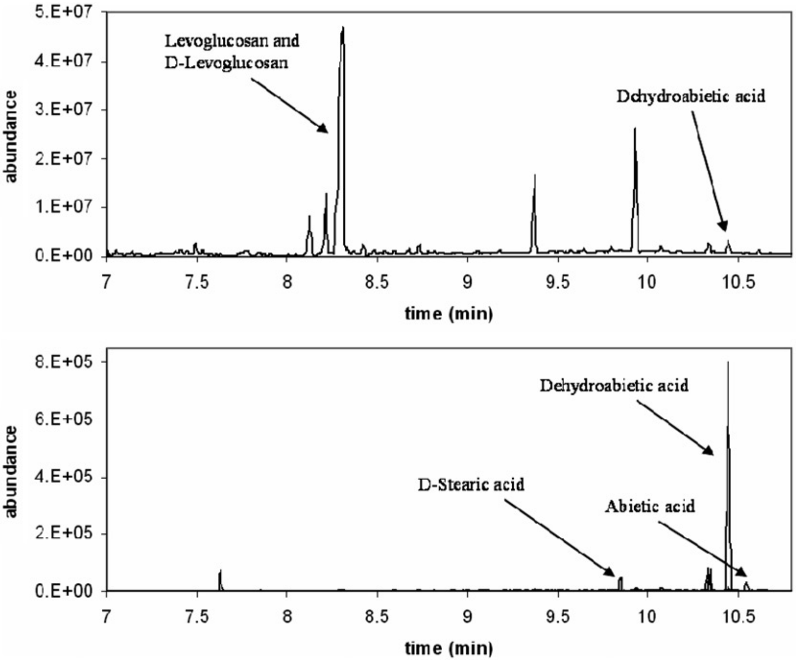

Figure 2. Total ion chromatogram (top) showing an example of a sample from Libby analysed for levoglucosan and resin acids and an extracted ion chromatogram (bottom), showing the specific ion peaks used to quantify the resin acids. The chromatograms were started at 7.00 minutes to eliminate the peaks from the derivatizing reagents.

Table 2. Recovery of compounds spiked onto blank filters ($n = 57$).

Compound	% recovery
Levoglucosan	105 ± 7.7
Dehydroabietic acid	64 ± 3.5
Abietic acid	60 ± 3.6
Vanillin	98 ± 3.2
Acetovanillone	102 ± 3.8
Guaiacol	104 ± 4.9
4-Ethylguaiacol	116 ± 4.7

amine [8,9,26], dichloromethane/methanol [15,22], methanol/water/dichloromethane [2,7], and hexane/benzene/proponal [2,1,27]. Soxhlet extraction using Hydromatrix, dichloromethane, and acetone has also been used to extract levoglucosan from particulate matter [28]. A comparison of the ethyl acetate and dichloromethane-based solvent systems showed no difference in their performance [28,29]. Ethyl acetate with triethylamine was chosen for this study because it does not utilise benzene, a known carcinogen, or dichloromethane, a suspected carcinogen [30]. Aqueous extraction has been reported for levoglucosan determination [31], but this method will not extract the methoxyphenols and resin acids as well. Protic solvents such as water and methanol are also not compatible with the derivatization conditions for levoglucosan and the resin acids.

A variety of different derivatization conditions were investigated for levoglucosan, dehydroabietic acid and abietic acid. Levoglucosan can be derivatized with TMSI [9], BSTFA/TMCS [7,15,17,22,31], or BSTFA/TMCS plus pyridine [3, 23, 24, 28, 29], while the resin acids are derivatized with a mixture of BSTFA and TMCS [2,7,22,24]. These compounds can also be analysed as their methyl ester derivatives [2,5,6,19,21,27].

The mixture of BSTFA/TMCS is a weaker set of conditions and typically requires heating for 3 + hours to completely derivatize levoglucosan from particulates. Under these conditions, several derivatization products of levoglucosan were frequently observed in our samples, suggesting the reaction was not going to completion. TMSI is a stronger reagent, and can derivatize both types of compounds, but causes much noisier peaks and appears to degrade the resin acids. A mixture of the three reagents (BSTFA/TMCS/TMSI) as well as a BSTFA/TMCS/pyridine mixture was investigated. Both were found to be effective at derivatizing the compounds in less than 60 minutes. The TMSI has the same function as the pyridine and also has additional trimethylsilyl groups that can react with the analytes. The first mixture was chosen because it contains a greater amount of silylating reagents and, therefore, should experience fewer problems with the varying amounts of unknown compounds present in wood smoke. We also found it necessary to evaporate the extracts to dryness before derivatization. When the solvent is not removed, levoglucosan is not completely derivatized under the chosen conditions.

The methoxyphenols can be analysed as trimethylsilyl derivatives, however this was not found to be optimal under our conditions. The current conditions for TMS derivatization require the solvent to be evaporated first. This is not favourable for the methoxyphenols because they are volatile and were found to evaporate with the solvent. To avoid these problems, a different set of derivatization conditions was used for the methoxyphenols, generating the acetate derivatives. Levoglucosan and the resin acids do not form acetate derivatives under the conditions used.

Derivatization conditions for the methoxyphenols were adopted from Simpson *et al.* [8]. The four chosen methoxyphenols all derivatize quickly, so the reaction time was reduced from 3 hours to 1 hour. Simpson's work suggests that the syringol type methoxyphenols require longer to derivatize than the others, so the time can be reduced when these compounds are not being analysed for. The original conditions of 50 µL of a 4:3 mixture of acetic anhydride: triethylamine produced double peaks of identical mass spectra on the chromatograms for both vanillin and guaiacol, for unknown reasons. The amount of derivatizing reagents was reduced to 30 µL of a 2:3 mixture in 250 µL of sample because this was found to be sufficient for the compounds to be analysed and did not produce the double peaks.

Some sample filters were extracted a second time to check the efficiency of the extraction procedure with a fresh volume of solvent and an additional 30 minutes of sonication. Levoglucosan was the only tracer detected after the second extraction, and all levels measured were less than 6% of the first extraction, so the extraction procedure was determined to be sufficient. Increasing the sonication time or volume of solvent also had little or no effect on the recovery.

Table 3. Detection limits of the seven selected tracers.

Compound	MDL (ng mL^{-1})	MDL (ng m^{-3} air)
Levoglucosan	185.0	7.7
Dehydroabietic acid	15.3	0.6
Abietic acid	11.9	0.5
Vanillin	20.7	0.9
Acetovanillin	12.8	0.5
Guaiacol	0.67	0.03
4-Ethylguaiacol	1.52	0.1

3.2 *Method characterization*

Detection limits for the method were defined as the concentration of analyte that gives an instrument response that is three times the magnitude of the instrument noise. The detection limit for each compound was calculated and is listed in Table 3.

Blank filters were spiked with known levels of all seven compounds and four deuterated internal standards and passed through the extraction procedure daily in parallel with the samples analysed. Recovery was calculated from these spiked filters to monitor method efficiency and instrument performance (see Table 2). The spike solutions were all prepared in ethyl acetate, except for levoglucosan, which was prepared in acetonitrile. Calibration standards were also made at least once a week to monitor solutions and instrument calibration.

The recoveries were close to 100% for levoglucosan, vanillin, acetovanillone, and guaiacol. 4-Ethylguaiacol had a recovery above 100%, which is due to a better recovery of this compound than its corresponding deuterated standard (D-guaiacol). The resin acids both exhibited recoveries that were significantly lower than 100%, but they were still reproducible. There is no isotope labelled resin acid commercially available and attempts to synthesise one were unsuccessful. D-35 stearic acid was chosen as a standard because it has the same functional group and similar molecular weight as the resin acids, but a different carbon backbone. We speculate that this difference in structure gave the standard different interactions with particulates and filters than the resin acids and caused a difference in extraction efficiency and recovery. However, a second extraction of the filters does not show any resin acids, so it is unlikely that the resin acids are remaining on the filter. The resin acids could also be remaining in the particles after extraction from the sample filter and are then being removed and discarded during filtration with the nylon membrane filter. Another possible explanation is incomplete derivatization of the resin acids under the current conditions. A longer derivatization time and stronger conditions were investigated, but no change in recovery was observed. While the exact cause of the low recoveries is unknown, the recovery for both resin acids was reproducible and the low recovery can thus be corrected for if desired. The results presented in this paper are corrected for recovery.

Field and lab blanks were analysed to monitor for contamination. The field blanks were stored with the samples to check for contamination in transport and storage, while the lab blanks were prepared daily at the same time as the samples to check for contamination in the analysis procedure. For every 10 filters that were analysed,

Table 4. Average values of the selected tracers and $PM_{2.5}$ measured in Libby, MT during the winter of 2004–05.

Compound	Average ($ng\,m^{-3}$ air)	95% confidence interval	*n* detected/ *n* total	Correlation to $PM_{2.5}$(R^2)	Slope of best fit line (ng analyte/ $ng\,g^{-1}$ PM)	Error of the slope (ng analyte/ $ng\,g^{-1}$ PM)
Levoglucosan	3040	675	18/18	0.7924	119	15
Dehydroabietic acid	364	70.6	18/18	0.7570	11.7	1.7
Abietic acid	30.3	9.45	18/18	0.8344	1.77	0.20
Vanillin	17.1	6.65	17/17	0.0023		
Acetovanillone	3.14	2.18	9/17	0.0149		
Guaiacol	4.27	3.35	18/18	0.1448		
4-Ethylguaiacol	0.67	0.46	18/18	0.0055		
$PM_{2.5}$	27.26 μg PM	4.61 μg PM	18			

one sample and one spiked blank filter were analysed in duplicate to check reproducibility (typically one of each per day of analysis).

Levoglucosan was detected on two of seven blank filters, but with an average concentration of only 124.6 $ng\,m^{-3}$, which is less than 5% of the average level measured on the samples. Dehydroabietic acid was detected at low levels on all seven of the blanks, but abietic acid was not detected on any of them. An average concentration of dehydroabietic acid on the blanks was determined and subtracted from every sample to correct for this. The levels of dehydroabietic acid detected on the blanks were less than 30% of the average levels measured on the samples. For the methoxyphenols, acetovanillone was not detected on any of the blanks; vanillin and 4-ethylguaiacol were detected at low levels on one blank and guaiacol on three. None of the blank filters were positive for more than four of the compounds, suggesting that contamination during transport or storage did not occur. The presence of different compounds on the blanks is likely due to small contamination during the sample preparation or analysis.

3.3 *Method application: Libby, MT*

The method developed was applied to ambient samples collected in Libby, MT during the winter of 2004–05. The average concentration of each tracer over the winter was determined (Table 4). A large range of day-to-day concentrations of all seven tracers was shown. The level of levoglucosan measured in Libby in this study was higher than levels measured in other US urban areas, such as Seattle, WA (13–760 $ng\,m^{-3}$) [9], Spokane, WA (2–327 $ng\,m^{-3}$) [26], and Fresno and Bakersfield, CA (23–7590 $ng\,m^{-3}$) [19]. Levels of vanillin and other methoxyphenols were difficult to compare to previously reported values due to differences in sample collection methods and the semi-volatile nature of these compounds [18]. The level of dehydroabietic acid measured in this study was significantly higher than the level reported in forest fire smoke collected in an urban environment [24].

Levoglucosan, dehydroabietic acid, and abietic acid were found to have a good correlation with $PM_{2.5}$ levels (Figures 3a and 3b). Since the majority of the $PM_{2.5}$ present in Libby was due to wood smoke, this result was expected. This suggests that these

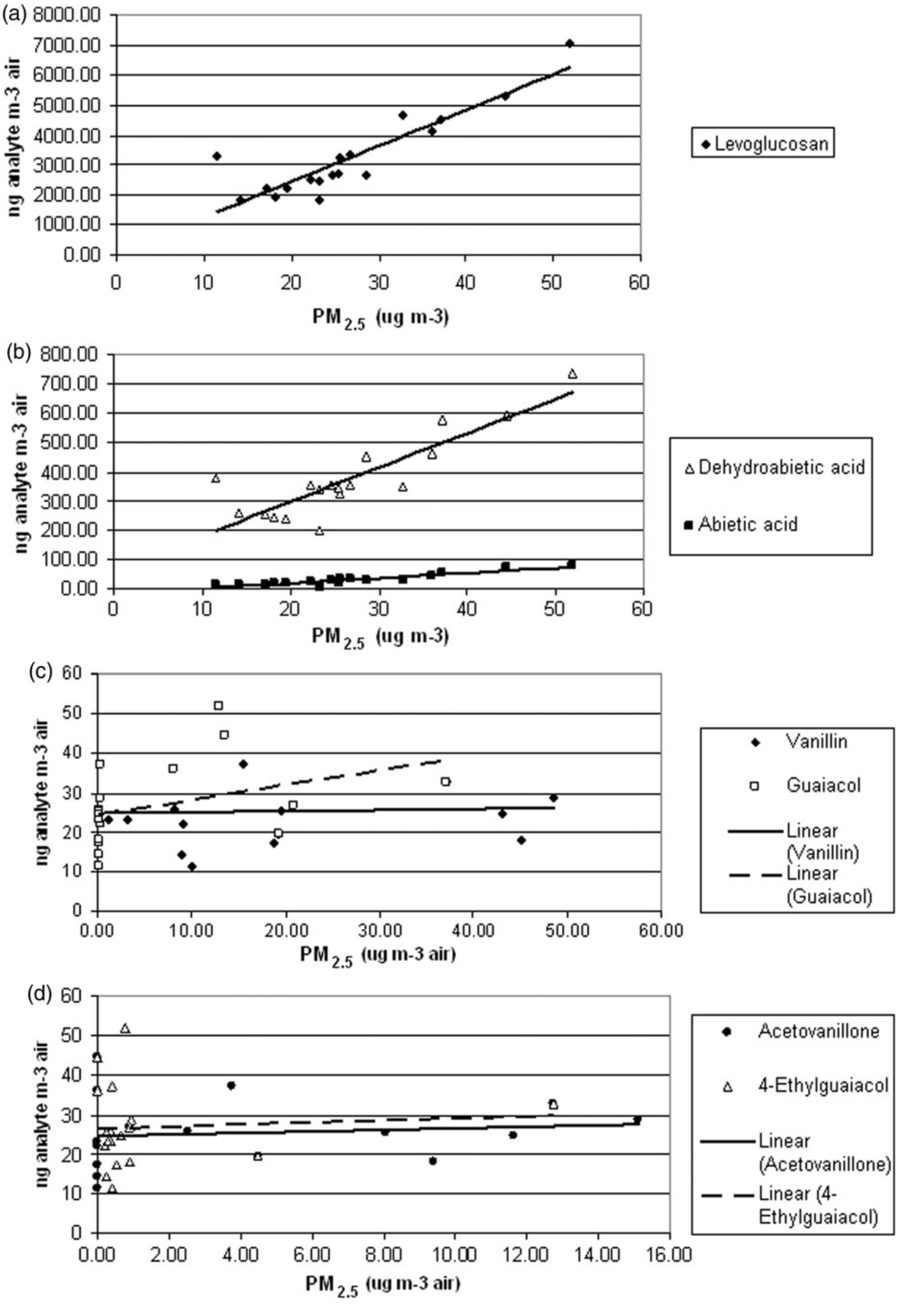

Figure 3. Correlation between levels of the selected tracers and $PM_{2.5}$ measured in Libby during the winter of 2004–05. Notes: a) levoglucosan ($R^2 = 0.7924$) b) dehydroabietic acid ($R^2 = 0.7570$) and abietic acid ($R^2 = 0.8344$) c) vanillin ($R^2 = 0.0023$) and guaiacol ($R^2 = 0.1448$) d) acetovanillone ($R^2 = 0.0149$) and 4-ethylguaiacol ($R^2 = 0.0055$).

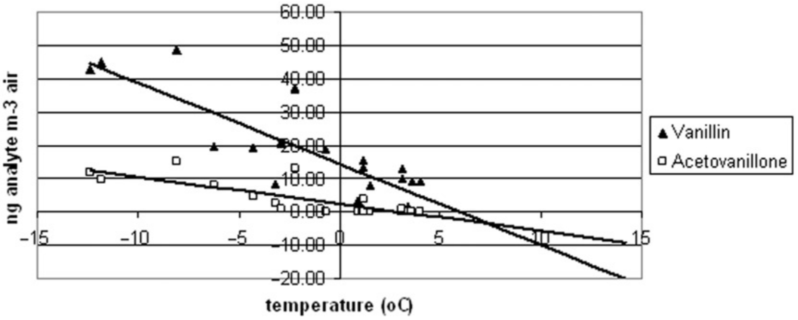

Figure 4. Correlation between levels of vanillin and acetovanillone and ambient air temperature on the day of sample collection measured in Libby during the winter of 2004–05. ($R^2 = 0.7009$ for vanillin and 0.6447 for acetovanillone.).

compounds are useful tracers for wood smoke in particulate matter. The slope of the association between $PM_{2.5}$ mass and each of these three compounds is reported in Table 4. These slopes indicate that levoglucosan represents about 11.9% of the $PM_{2.5}$ mass, while dehydroabietic acid accounts for about 1.2% and abietic acid is about 0.2%. Previously reported values of the ratio of levoglucosan to PM in fireplace emissions are 0.8–26% [2,27]. Reported values for dehydroabietic acid range from 0.3–8.7% and value for abietic acid range from 0.1–1.6% [5,6,21,32]. Most of the reported values are from the burning of specific species of wood, such as ponderosa or loblolly pine, which can produce different ratios of the resin acids than the larch and Douglas fir burned in Libby.

In this study, the levels of all four methoxyphenols measured showed poor correlation with $PM_{2.5}$, suggesting that these four compounds are not suitable tracers for wood smoke in this setting (Figures 3c and 3d). Other methoxyphenols, such as propionylsyringol and butyrylsyringol, have been successfully used in a source apportionment model for PM [19]. However, neither of these compounds were measured in the original chemical profile of the Libby particulate matter [1].

During a typical Libby winter, temperature inversions frequently occur for extended periods on time, allowing for $PM_{2.5}$ emitted from valley sources to build up in the airshed. These temperature inversions are characterised by cold temperatures, low winds, and high humidity (fog). In an effort to investigate whether the measured concentrations of the analytes of interest were dependent on such meteorological conditions, the measured levels of all seven compounds were compared to meteorological parameters (including temperature, wind speed and direction, barometric pressure, daily precipitation (snowfall), and snowfall accumulation) for each of the sample days. Due to the size of the community and the limited resources dedicated to the existing meteorological monitoring station, the number of parameters that are continuously measured in Libby is limited. For example, relative humidity, which is one indicator of temperature inversions, was not measured in Libby during the winter of 2004–05. In investigating the relationships between meteorological conditions and the concentrations of analytes measured in this study, the only correlation found was an inverse relationship between temperature and the levels of vanillin and acetovanillone (Figure 4). $PM_{2.5}$ levels, levoglucosan, dehydroabietic acid, and abietic acid did not show a direct relationship to any of the measured meteorological parameters.

Due to the absence of correlation between the majority of our measured compounds and meteorological conditions, we speculate that the correlation between the vanillin compounds and temperature is due to their high volatility, resulting in higher fractions of these compounds in the particle phase at low temperatures. Guaiacols are also volatile, but no trend was seen, possibly due to the very low levels at which they are present. The levels of these four methoxyphenols measured in the particulate phase are likely to be a function of both analyte concentration and temperature at the time of sample collection.

4. Conclusions

A method was developed for the determination of chemical tracers for biomass burning in particulate matter. The method provides excellent recoveries for levoglucosan, vanillin, acetovanillone, guaiacol, and 4-ethylguaiacol and adequate and reproducible recoveries for dehydroabietic acid and abietic acid. The sensitivity and precision of the method are good for all of the selected compounds. The method was applied to ambient $PM_{2.5}$ quartz filter samples collected in Libby, MT, as an example of a community that experiences significant exposure to wood smoke particulates. The concentrations of levoglucosan and the two resin acids were found to correlate strongly with the levels of $PM_{2.5}$ from this community. The fraction of the $PM_{2.5}$ mass corresponding to levoglucosan and the resin acids was within the range of previously reported values for wood smoke dominated particulate matter. However, the levels of the semivolatile methoxyphenols in the PM were not correlated with levels of $PM_{2.5}$, but were affected by the ambient temperature. Under these sampling conditions, levoglucosan, dehydroabietic acid, and abietic acid are suitable tracers for wood smoke in $PM_{2.5}$.

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