

## RESEARCH ARTICLE

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## Key Points:

- RWC was found to be a substantial source of gas phase air toxics in wintertime
- The MLR model results suggest that MOVES was overpredicting mobile source emissions of CO relative to NO<sub>x</sub> by a factor of 1.33
- MOVES was overpredicting mobile source emissions of black carbon relative to NO<sub>x</sub> by a factor of 3

## Supporting Information:

- Supporting Information S1

## Correspondence to:

B. Jobson,  
tjobson@wsu.edu

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## Contributions of wood smoke and vehicle emissions to ambient concentrations of volatile organic compounds and particulate matter during the Yakima wintertime nitrate study

Graham VanderSchelden<sup>1</sup> , Benjamin de Foy<sup>2</sup> , Courtney Herring<sup>1</sup>, Susan Kaspari<sup>3</sup> , Tim VanReken<sup>1</sup> , and Bertram Jobson<sup>1</sup> 

<sup>1</sup>Laboratory for Atmospheric Research, Department of Civil and Environmental Engineering, Washington State University, Pullman, Washington, USA, <sup>2</sup>Department of Earth and Atmospheric Sciences, Saint Louis University, St. Louis, Missouri, USA, <sup>3</sup>Department of Geological Sciences, Central Washington University, Ellensburg, Washington, USA

**Abstract** A multiple linear regression (MLR) chemical mass balance model was applied to data collected during an air quality field experiment in Yakima, WA, during January 2013 to determine the relative contribution of residential wood combustion (RWC) and vehicle emissions to ambient pollutant levels. Acetonitrile was used as a chemical tracer for wood burning and nitrogen oxides (NO<sub>x</sub>) as a chemical tracer for mobile sources. RWC was found to be a substantial source of gas phase air toxics in wintertime. The MLR model found RWC primarily responsible for emissions of formaldehyde (73%), acetaldehyde (69%), and black carbon (55%) and mobile sources primarily responsible for emissions of carbon monoxide (CO; 83%), toluene (81%), C<sub>2</sub>-alkylbenzenes (81%), and benzene (64%). When compared with the Environmental Protection Agency's 2011 winter emission inventory, the MLR results suggest that the contribution of RWC to CO emissions was underestimated in the inventory by a factor of 2. Emission ratios to NO<sub>x</sub> from the MLR model agreed to within 25% with wintertime emission ratios predicted from the Motor Vehicle Emissions Simulator (MOVES) 2010b emission model for Yakima County for all pollutants modeled except for CO, C<sub>2</sub>-alkylbenzenes, and black carbon. The MLR model results suggest that MOVES was overpredicting mobile source emissions of CO relative to NO<sub>x</sub> by a factor of 1.33 and black carbon relative to NO<sub>x</sub> by about a factor of 3.

### 1. Introduction

A comprehensive air quality study was performed during January 2013 to investigate sources of air pollution in Yakima, WA. Particulate matter (PM<sub>2.5</sub>) concentrations in the region have approached the Environmental Protection Agency (EPA) 24 h standard in recent years, with the highest PM<sub>2.5</sub> days occurring during wintertime. Residential wood combustion and vehicles are the major wintertime sources of particulate matter (PM) and toxic air pollutants in Yakima according to the 2011 National Emissions Inventory (NEI). While the Motor Vehicle Emission Simulator (MOVES) 2010b model is an established method for estimating emissions from mobile sources [Environmental Protection Agency, 2010], the emission inventory for residential wood combustion is not as well constrained. This uncertainty stems from the difficulty in quantifying wood combustion activity levels that are often determined using community surveys, which are expensive and quickly outdated due to changes in populations and device usage [Tian *et al.*, 2004]. Residential wood combustion has been found to be a major source of ambient PM<sub>2.5</sub> in wintertime in a variety of different air sheds [Maykut *et al.*, 2003; Ward *et al.*, 2006; Alfarra *et al.*, 2007; Lanz *et al.*, 2008; Ward and Lange, 2010], but its role as a source of air toxics has received much less attention. Quantifying the role of residential wood combustion as a multipollutant source relative to other sources of air pollution is important for health impact assessments of wood combustion. Chemical mass balance modeling provides a straightforward means to assess source contributions in air sheds dominated by only a few sources, allowing air quality managers to clearly identify solutions for management of wintertime air quality and articulate these strategies to the community.

The wintertime 2011 NEI provided the most recent emission estimates for comparison to findings of this study. Emission estimates were compiled by the Washington State Department of Ecology (WSDOE), and a description of the emission estimation process is available in WSDOE's 2011 Emissions Inventory

Documentation [WSDOE, 2013]. Mobile source emissions were determined by WSDOE using the MOVES model version 2010b, utilizing a hybrid of specific local data from state and local agencies mixed with EPA default inputs. The procedure for assembling the emission inventory for residential wood smoke was more complicated, leaving more room for uncertainty. The residential wood smoke inventory was developed using activity levels from a 2007 survey on wood-burning device usage in western Washington from the National Research Center (NRC) and using emission factors from the EPA's 2011 residential wood combustion tool. Emission factors are reported in the 2011 Emissions Inventory Documentation [WSDOE, 2013]. Yakima county wood-burning device usage rates were compiled from averaged NRC survey results from Pierce, Kitsap, and Snohomish Counties. Device usage rates, fuel usage rates, percentage of devices that were EPA certified, and percentage of EPA-certified devices that were catalytic were all determined using survey data, industry data, and assumptions on fuel dry weight for common wood quantity units (such as chords, bundles, and pickup loads). Emission factors from the EPA's residential wood combustion tool were reported across all device types for all criteria pollutants but were only provided for a few air toxics and not comprehensively across all device types. Residential wood combustion emissions were allocated seasonally: 68%, 20%, 13%, and 0% for winter, fall, spring, and summer, respectively. These emission rates are incorporated into the emission inventory used in hourly chemical forecasts for the Pacific Northwest region using the Air Indicator Report for Public Awareness and Community Tracking (AIRPACT) version 4 model system [Vaughan *et al.*, 2004].

Lack of available survey data or observations of residential wood-burning activity are the primary reason for uncertainties in the emission inventory. In this case, the counties for which survey data were used by WSDOE are located in western Washington, across the Cascade Mountains. Survey data from Pierce, Kitsap, and Snohomish Counties were used to develop the residential wood combustion emission estimates for the 2011 National Emissions Inventory which is referenced in this paper. This is a potential source of uncertainty in the inventory since the climate is different in Yakima County than in any of the three counties from where survey data were used. The mean January temperature from 1981 to 2013 was  $-0.4^{\circ}\text{C}$  in Yakima County but  $4.8^{\circ}\text{C}$ ,  $5.9^{\circ}\text{C}$ , and  $4.9^{\circ}\text{C}$  in Kitsap, Pierce, and Snohomish Counties, respectively. Colder temperatures in Yakima suggest that more wood is likely to be burned for heating per household than in the warmer counties. Additionally, the income demographic is different in Yakima County than the other three. The median household income from the American Community Survey 2013 was \$43,506 for Yakima County, while it was \$62,413, \$59,204, and \$68,381 for Kitsap, Pierce, and Snohomish Counties, respectively. Differences in income levels could indicate differences in home heating fuel use. Interestingly, American Community Survey 2011–2013 estimates that 4.9% of household units in Yakima County use wood for home heating, while the WSDOE estimate for the NEI was that 31.6% of households use wood-burning devices. This discrepancy is likely because WSDOE was estimating the percentage of wood-burning devices used, while the American Community Survey was tabulating percentage of households that utilize wood as their primary source of heat.

In this paper, a two-source chemical mass balance model using multiple linear regression (MLR) analysis [de Foy and Schauer, 2015] was applied to determine the contributions of residential wood combustion and mobile sources to ambient concentrations of carbon monoxide (CO), a few organic air toxics, organic PM, and black carbon. The results from the chemical mass balance models were compared to MOVES model output for on-road vehicles and wood smoke emission ratios from the literature. The goal of this study was to determine the relative contribution of residential wood combustion and mobile sources on wintertime air pollutants for comparison to the emission inventory.

## 2. Experiment

### 2.1. Site Description

The Yakima Wintertime Nitrate Study took place from 5 to 27 January 2013 in Yakima Washington to assess the air pollution sources and wintertime meteorology that cause elevated wintertime  $\text{PM}_{2.5}$  [VanReken *et al.*, 2014]. Yakima is a relatively small city with an estimated population of 93,357 in 2013, located in the Upper Yakima Valley. The Upper Yakima Valley is bordered by the Cascade Mountains to the west and hills to the north and south that rise about to a 200 m height above the valley floor. These hills come together in the east to form an enclosed basin that restricts airflow, especially when inversion heights are low. Due to its location in the rain shadow of the Cascades, Yakima's climate is classified as semiarid. January weather is characterized

by average high and low temperatures of 3.8°C and −4.6°C and 28.7 mm of precipitation on average (1981–2010 mean) [VanReken *et al.*, 2014]. During January 2013, temperatures were close to their historical averages with average highs and lows of 3.4°C and −4.4°C, respectively. However, 2013 saw a much drier January than usual, with only 2.5 mm of recorded precipitation [VanReken *et al.*, 2014].

Instrumentation used in this study was housed in the Laboratory for Atmospheric Research Mobile Atmospheric Chemistry Lab (MACL). The MACL is a 6 m long climate-controlled trailer with a 10 m tall crank-up tower designed to accommodate instruments and inlets. The MACL was deployed on the softball field at the Campus of Yakima Valley Community College (46.58854°N, 120.5283°W; elevation 327 m). This site was about 40 m south of Arlington Road, which was used primarily for student parking. The major arterials are South 16th Ave and West Nob Hill Blvd 150 m west and 400 m south of the site, respectively. The site was located in a mixed residential and commercial neighborhood about 2 km southwest of the urban center. There were significant wood smoke emissions visible from chimneys of nearby residences, suggesting that many houses used wood fuel for home heating.

## 2.2. Instrumentation

Gas phase sampling for carbon dioxide (CO<sub>2</sub>), ozone (O<sub>3</sub>), CO, and volatile organic compound (VOC) instruments was performed through a common 1/2" outer diameter (OD) perfluoroalkoxy sample line with a funnel on the inlet end to protect against snow and rain. The inlet for the common sample line was positioned on top of the 10 m tower, and air was pulled through the line at approximately 30 liters per minute; instruments in the trailer were subsampled from this flow. A proton transfer reaction–mass spectrometer (PTR-MS; Ionicon Analytik, Austria) was used to measure VOCs and is described in detail in the literature [Lindinger *et al.*, 1998; de Gouw and Warneke, 2007]. The PTR-MS was operated in concert with a sample dehumidifier, described in detail by Jobson and McCoskey [2010]. Dehumidifying sample air limits the amount of clustering of ambient water vapor with H<sub>3</sub>O<sup>+</sup> ions, allowing the PTR-MS to be operated at 80 Td ( $U_{\text{drift}} = 328 \text{ V}$ ,  $P_{\text{drift}} = 2.08 \text{ mbar}$ , and  $T_{\text{drift}} = 65^\circ\text{C}$ ) to reduce fragmentation and to enhance sensitivity. The PTR-MS response was calibrated using an external compressed air standard (Scott Marrin) containing 13 components with a stated accuracy of ±5%. The instrument response to formaldehyde was determined using a permeation device (Kin Tek). CO was measured using a vacuum UV fluorescence instrument (Aerolaser, Germany), and response was calibrated to a CO standard (Scott Marrin, 1% accuracy). Nitrogen oxide (NO<sub>x</sub>) measurements were made using a two-channel NO<sub>x</sub>/NO<sub>y</sub> chemiluminescence analyzer (Air Quality Design, USA). The NO<sub>x</sub>/NO<sub>y</sub> inlet system was mounted on the tower about 4 m below the other gas phase inlet in a National Electrical Manufacturers Association enclosure. The inlet system consists of flow controllers, a molybdenum catalyst for converting NO<sub>y</sub> to NO, and a photolysis cell for conversion of NO<sub>2</sub> to NO. Sample air was drawn from the inlet box into the MACL through 0.25" OD tubing to be analyzed by the main instrument. One channel of the instrument was dedicated to making continuous NO<sub>y</sub> measurements. The other channel was dedicated to making NO<sub>x</sub> measurements, with sample air passing through the NO<sub>2</sub> photolysis cell and having the lamp toggled on and off every 30 s. NO mixing ratios were measured when the lamp was off, while NO<sub>2</sub> mixing ratios were calculated from the difference in signal of lamp-on periods and lamp-off periods.

The aerosol inlet was positioned on the tower about 3 m below the main gas phase inlet. The particle inlet system consisted of a 0.5" copper tube wrapped in heating tape that was thermostated to 10°C to prevent ice buildup in the inlet system. The flow rate through the aerosol inlet was 4 liters per minute. The aerosol sample flow was passed through a Nafion dehumidifier to dry particles prior to sampling to allow easier intercomparison of the different aerosol measurements. Black carbon mass in individual particles between ~80 and 650 nm was measured using a Single-Particle Soot Photometer (SP2) [Schwarz *et al.*, 2006], following the SP2 alignment adjustment and calibration recommendations made by Laborde *et al.* [2012]. The composition of submicron nonrefractory particulate matter was measured by a high-resolution time-of-flight aerosol mass spectrometer (AMS; Aerodyne, USA). A detailed description of the AMS is available in the literature by DeCarlo *et al.* [2006]. The AMS is capable of separating and detecting semivolatile components of aerosols including sulfate, nitrate, ammonium, chloride, and total organic matter. The AMS cannot detect nonvolatile PM, black carbon, and crustal elements, for example. The AMS was calibrated in the field including a lens alignment, flow calibration,  $m/z$  calibration, and particle size calibration at the beginning of the study. Ionization efficiency calibrations were performed at the beginning, middle, and end of the study,

and  $m/z$  calibration and tuning was performed daily. AMS detection limits were determined from five filter collections and are shown in Table S1 in the supporting information.

### 2.3. Chemical Mass Balance Model

A chemical mass balance model for source apportionment uses a linear combination of tracer compounds to reconstruct the ambient concentration of a pollutant. The chemical mass balance model concept is described in detail in the literature [Friedlander, 1973; Watson, 1984; Watson *et al.*, 1990; Fujita *et al.*, 1994]. The general form of the chemical mass balance equation is shown in equation (1):

$$C = \sum E_i \cdot T_i \quad (1)$$

where  $C$  is the measured pollutant concentration, which is assumed to be a result of contribution from some fixed number of sources  $n$ , whose relative contributions to the measured amount can change with time. The contributions of each source  $i$  can be accounted for by measuring a unique tracer of that source  $T_i$ . The contribution of the source to the measured pollutant  $C$  is accounted for by the emission factor  $E_i$ , which is the amount of pollutant  $C$  emitted per unit of tracer compound  $T$ .

This approach can work if the pollutants are conserved and not lost by atmospheric processing during the time scale from emission to measurement. In Yakima, the 2011 wintertime county emission inventory suggests that there are only two significant sources of CO, NO<sub>x</sub>, VOCs, and semivolatile PM: residential wood burning and mobile sources. The winter season 2011 county-level emission inventory for CO and NO<sub>x</sub> shows that mobile sources are responsible for 90% and 95% of anthropogenic emissions, respectively. Wood smoke is responsible for 10% of CO and 2% of NO<sub>x</sub>. For PM<sub>2.5</sub>, the winter emission profile is dominated by wood smoke and mobile sources if road dust, construction dust, agricultural tilling, and outdoor burning are ignored. Ignoring these components for the chemical mass balance model approach is reasonable because the AMS instrument is unable to measure nonvolatile crustal elements, meaning that road dust, construction dust, and agricultural tilling will not show up in AMS measurements of PM. Additionally, burn bans were in effect during the study that prohibited outdoor burning, principally of agricultural waste. VOC emissions are dominated by wood combustion and mobile sources in the emission inventory. However, smaller influences from solvents/gasoline fuel transport/storage/filling stations could complicate the chemical mass balance model approach for some organics.

Given the predominance of residential wood combustion and mobile sources in the emission inventory we used a two-component chemical mass balance model using acetonitrile (CH<sub>3</sub>CN) and NO<sub>x</sub> as the source tracers. Acetonitrile has been shown to be a good general tracer compound of biomass burning, as acetonitrile mixing ratios are enhanced in biomass-burning plumes but do not show a significant increase in urban or power plant plumes [de Gouw *et al.*, 2003]. Acetonitrile has been used as a biomass-burning marker in many other studies to track forest biomass-burning plumes [de Gouw *et al.*, 2003; Karl *et al.*, 2007; Yokelson *et al.*, 2009; Lack *et al.*, 2013] and agricultural burning [Holzinger *et al.*, 2005; Yokelson *et al.*, 2009; Yuan *et al.*, 2010]. Acetonitrile does have some emission from motor vehicle exhaust, as suggested by Holzinger *et al.* [2001]. To assess this potential influence, we used data from our own direct measurements of motor vehicle exhaust emissions [Erickson *et al.*, 2014]. These data show ~0.4% emission ratio of acetonitrile to toluene for gasoline engine exhaust. Given the measured abundance of toluene, and assuming that all toluene was from vehicles, the contribution from traffic sources is estimated to be less than 5% of the measured acetonitrile abundance in Yakima. For NO<sub>x</sub>, given the 2014 emission inventory distribution, mobile sources are responsible for 95% of the NO<sub>x</sub> emissions and wood smoke is responsible for around 2%. Although there is some contribution from each source to each tracer, the contributions are estimated to be small, and thus, the tracers are a relatively unique identifier of their respective major source.

During the model period NO<sub>x</sub> made up 93% of NO<sub>y</sub> on average, suggesting that NO<sub>x</sub> was well conserved. In wintertime, photochemical loss of VOCs and NO<sub>2</sub> from the air shed is thought to be insignificant. Photochemical modeling of wintertime urban air chemistry in this region using the AIRPACT forecast model system [Chen *et al.*, 2008] indicates average daytime HO concentrations of  $2 \times 10^5$  molecules/cm<sup>3</sup> during clear-sky conditions, resulting in an NO<sub>2</sub> lifetime of ~60 h, much longer than travel times across the town assuming low  $1 \text{ m s}^{-1}$  wind speeds (~3 h). The photochemical lifetimes of the tracers and other pollutants are long compared to transport times in the air shed and are thus considered reasonably well conserved

for chemical mass balance modeling. With the two sources defined, the chemical mass balance model applied to the data is shown in equation (2):

$$[C_{\text{poll}}] = C_o + E_{\text{ws}} \cdot [\text{CH}_3\text{CN}] + E_{\text{mob}} \cdot [\text{NO}_x] \quad (2)$$

where  $[C_{\text{poll}}]$  is the pollutant mixing ratio,  $E_{\text{ws}}$  is the emission ratio for wood smoke relative to acetonitrile,  $E_{\text{mob}}$  is the emission ratio for mobile source emissions relative to  $\text{NO}_x$ , and  $C_o$  is the amount unattributed to either source. Because CO and acetonitrile are long-lived in the atmosphere, regional backgrounds were removed from the time series for these species so that time series used in the chemical mass balance model would be representative of the enhancement caused by local emissions. Regional backgrounds for CO and acetonitrile are defined below in section 3.1.

The chemical mass balance model concept was executed using a multiple linear regression (MLR) model developed by *de Foy and Schauer* [2015]. The emission ratios were obtained by applying a least squares inversion directly to the concentration time series. Because the least squares method is sensitive to outliers, we use an iteratively reweighted least squares (IRLS) procedure. Residuals of the fit were calculated after each iteration of the multiple linear regression process and points were removed that had residuals higher than 2 standard deviations of the residuals. After two iterations the method converged on a stable set of outliers and the emission ratios were calculated from the remaining data points. The distributions of the data for many compounds were lognormal. An initial IRLS analysis was done on the log-transformed data. This procedure produced residuals that were normally distributed and allowed for a clear identification of outliers based on the  $2\sigma$  deviation criteria. The results of the log-transformed method in terms of goodness of fit and outlier identification were similar (see Table S2) and provided a level of quality assurance in the IRLS procedure. The regression coefficients determined from the log-transformed data are more difficult to interpret, whereas the untransformed data yield regression coefficients that are molar ratios and thus can be easily compared to emission inventories.

Uncertainty in the emission factors was estimated using the block-bootstrap procedure [*de Foy and Schauer*, 2015]. One-hundred realizations of the regression were simulated by randomly selecting individual hours to be included in the analysis. For each hour selected by the bootstrap, all the data points in that hour were included in the regression. When performing bootstrapping, the selection was done with replacement so that the total number of hours included in the analysis was unchanged but some hours were included more than once, whereas other hours may be left out. The uncertainty was reported as the standard deviation of the emission factors calculated by the 100 MLR realizations.

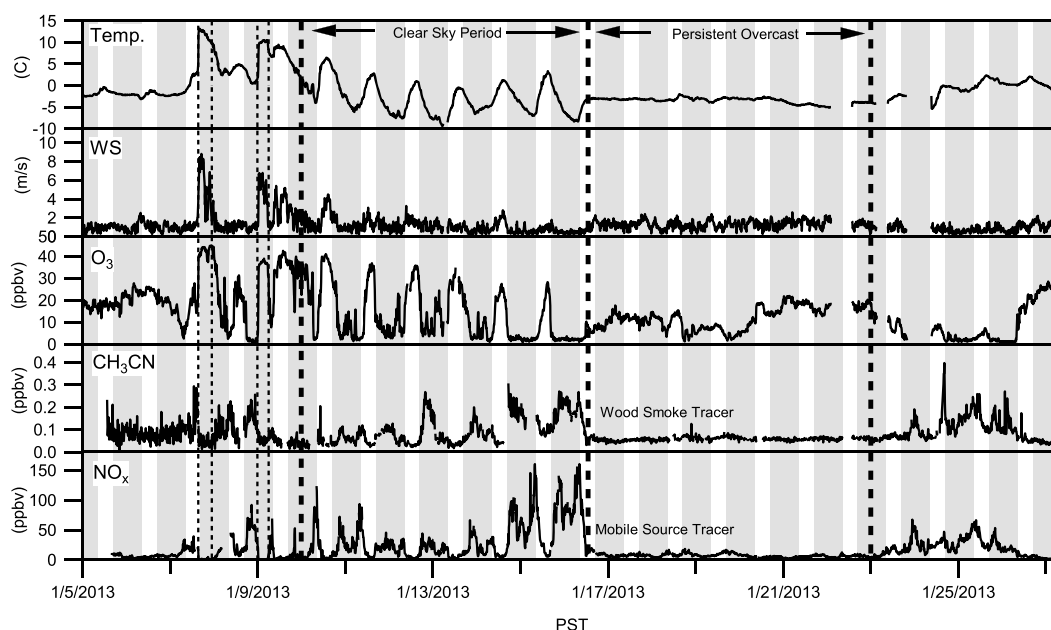
### 3. Results

#### 3.1. Regional Backgrounds

The backgrounds for CO and acetonitrile were determined by averaging mixing ratios during periods of high winds on 7 January (WNW flow at 7.5 m/s) and 9 January (SW flow at 5.4 m/s). These periods are depicted in the pollutant time series shown in Figures 1 and 2. The high-wind speeds ensured a well-ventilated air shed, whose composition reflects the regional background. The lowest levels of CO and acetonitrile during the campaign were observed during this windy period: for 7 January,  $\text{CO} = 133 \pm 5$  ppbv and  $\text{CH}_3\text{CN} = 44 \pm 17$  parts per trillion by volume (pptv) and for 9 January,  $\text{CO} = 118 \pm 3$  and  $\text{CH}_3\text{CN} = 52 \pm 13$  pptv. The differences in the CO background mixing ratios likely reflect differences in air mass origin given differences in synoptic-scale airflow. The larger uncertainty for acetonitrile reflects measurement precision at these low mixing ratios. The low level of acetonitrile compares well with acetonitrile measurements ( $56 \pm 20$  pptv) reported from a location near Tucson, AZ, in September [*Snider and Dawson*, 1984]. This acetonitrile background was significantly lower than the background that has been observed in many other studies of about 100–400 pptv [*Karl et al.*, 2002; *Jost et al.*, 2003; *Yuan et al.*, 2010]. Differences between studies may reflect seasonal and regional variations. For the analysis period, where wind flow typically had a more southerly component, we used the 118 ppbv CO background value and a 40 pptv background value for acetonitrile, which resulted in positive but near-zero values of  $\text{CH}_3\text{CN}$  in the afternoons.

#### 3.2. Data Selection for the Chemical Mass Balance Model

The chemical mass balance model was run for a clear-sky period during the beginning of the study, where there was significant variability of pollutants and tracer species due to meteorological variation (mixing

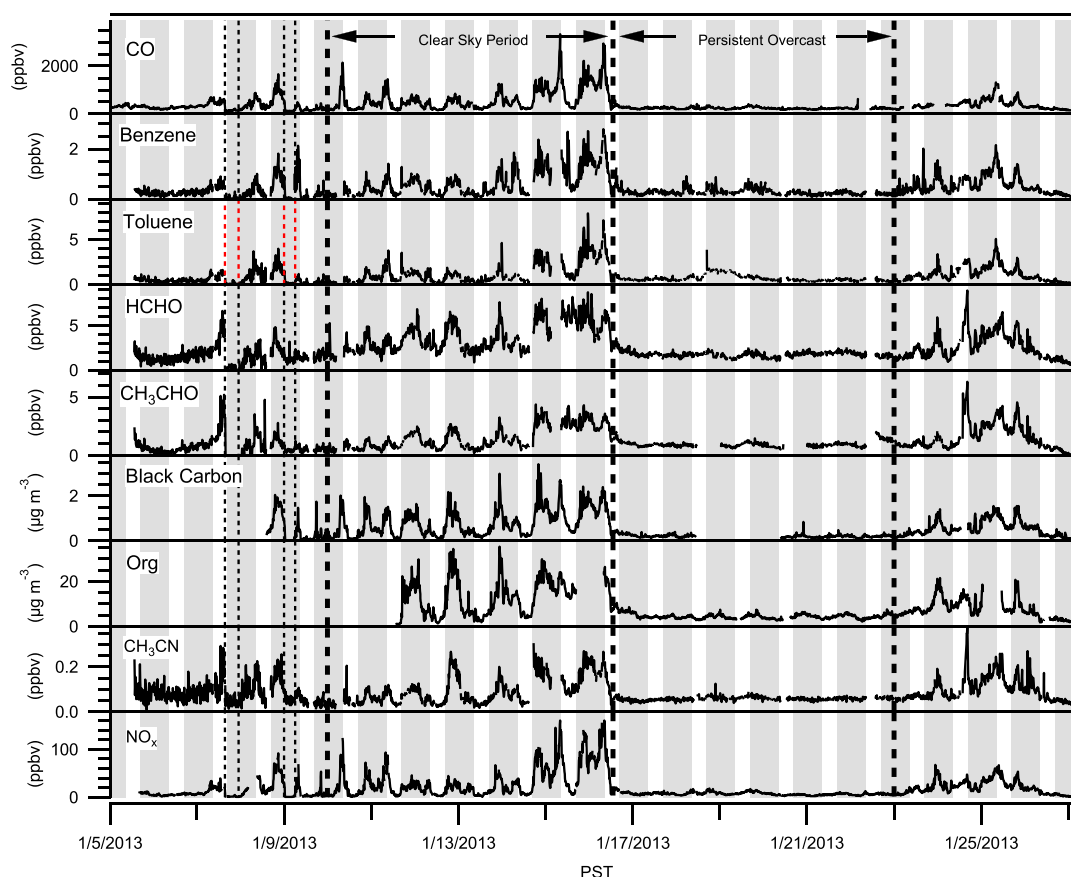


**Figure 1.** Time series of temperature, wind speed, ozone, acetonitrile (wood smoke tracer), and NO<sub>x</sub> (mobile source tracer). The areas denoted by dashed lines on 07 and 09 January indicate the high-wind period, during which regional back-grounds were determined for CO and CH<sub>3</sub>CN. Shaded areas indicate nighttime and unshaded areas indicate daytime.

height variation). This was a 5 day period from 11 January (00:00) to 16 January (00:00). This period was characterized by sunny skies, significant diel temperature variation, and low to moderate winds. Figure 1 displays the time series of temperature, wind speed, ozone, acetonitrile, and NO<sub>x</sub> for the whole study with the period used for the chemical mass balance model indicated. Figure 2 shows the time series of CO, benzene toluene, formaldehyde, acetaldehyde black carbon, and organic PM<sub>1</sub>. A typical diel pattern was observed: elevated concentrations in the mornings, decreasing into the afternoon as the boundary layer expanded, and increasing again in the late afternoon to early evening as a surface inversion layer forms. On 15 and 16 January wind speeds were very low, producing a stagnation event and the highest pollutant concentrations for the study period. Starting midmorning on 16 January clear skies gave way to an extended overcast period of persistent stratus cloud cover that produced very low and much more constant primary pollutant concentrations. The chemical mass balance model was run to perform source attribution for CO, formaldehyde, acetaldehyde, benzene, toluene, C<sub>2</sub>-alkylbenzenes, black carbon, and organic PM<sub>1</sub>.

### 3.3. Results of the Chemical Mass Balance Model

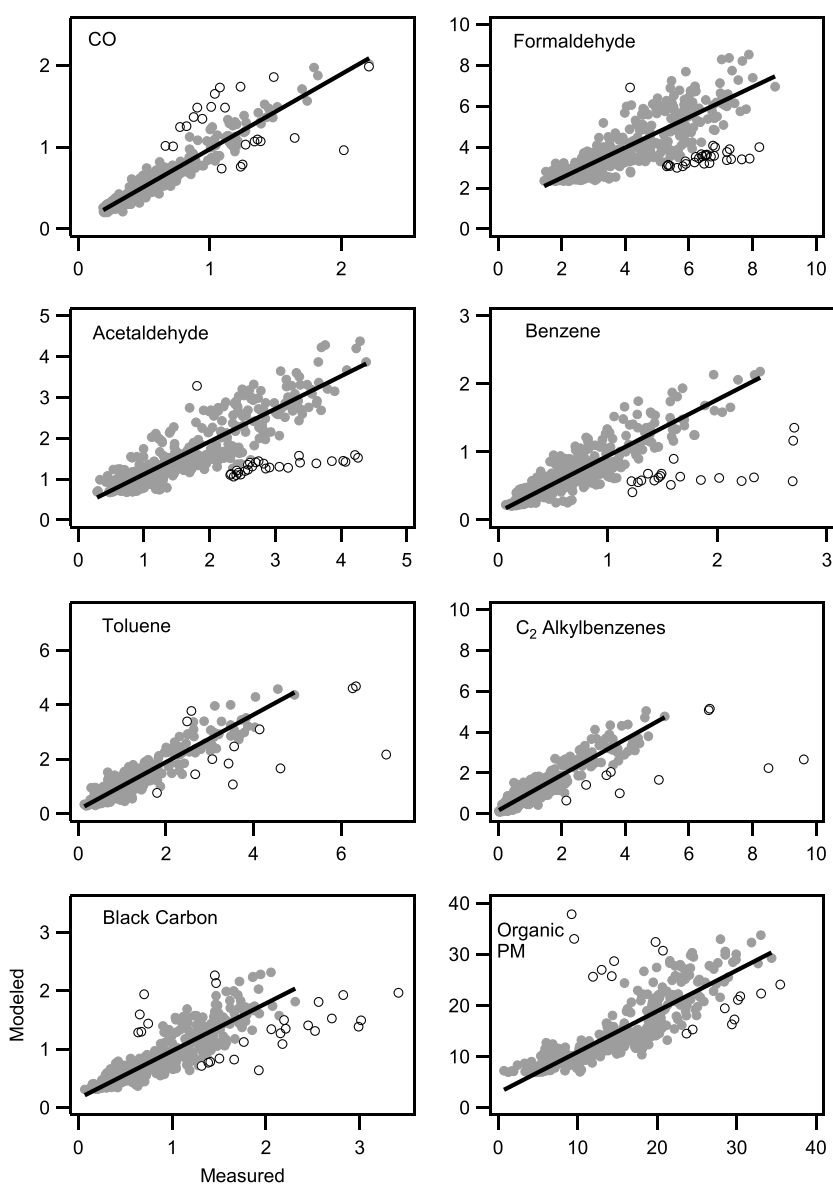
The MLR model produced results that closely followed observations for primary pollutants, implying that residential wood combustion and mobile sources were the dominant emission sources impacting the site. For CO, benzene, toluene, C<sub>2</sub>-alkylbenzenes, and black carbon, pollutants which are thought to be mostly primary emissions from wood smoke and mobile sources, the slope and  $r^2$  values for the modeled to measured correlations were between 0.81 and 0.93 as shown in Figure 3 and Table 1 (factors from the log-transformed data are shown for reference in Table S3). Table 1 also shows the regression coefficients (emission ratios). The high  $r^2$  values indicate that the chemical mass balance model did a good job of capturing the trend as well as the overall magnitude of these primary pollutant concentrations. Interestingly, for the pollutants that could potentially have secondary sources from atmospheric chemical processing (formaldehyde, acetaldehyde, and organic PM<sub>1</sub>), the measured to modeled comparisons yielded poorer correlations with slope and  $r^2$  values of 0.74 to 0.80. Poorer correlations along with the large intercepts ( $C_0$ ) of the formaldehyde and organic PM<sub>1</sub> correlations suggest that additional sources or processes contributed to the abundances of these pollutants. For these compounds the model reproduced morning and evening abundances reasonably well but underpredicted the afternoon abundance. Additional figures showing temporal dependence of the source attribution and model residuals are given in the supporting information.



**Figure 2.** Time series of PTR-MS measurements of CO, benzene, toluene, formaldehyde, acetaldehyde, black carbon, organic PM<sub>1</sub>, acetonitrile, and NO<sub>x</sub> for the entire campaign. The areas denoted by dashed lines on 07 and 09 January indicate the high-wind period, during which regional backgrounds were determined for CO and CH<sub>3</sub>CN. Shaded areas indicate nighttime and unshaded areas indicate daytime.

The higher abundances of HCHO, CH<sub>3</sub>CHO, NO<sub>3</sub><sup>-</sup> PM<sub>1</sub>, and organic PM<sub>1</sub> than predicted by the primary source tracers in the afternoon suggest secondary sources, somewhat surprising for this wintertime environment. The afternoon deviations were apparent for two afternoons during the strong stagnation period, as illustrated in Figure 4, which shows time series of HCHO, organic PM<sub>1</sub>, and NO<sub>3</sub><sup>-</sup> PM<sub>1</sub> for 14 and 15 January. The simultaneous increase of surface air temperature, odd oxygen (O<sub>3</sub> + NO<sub>2</sub>), and NO<sub>3</sub><sup>-</sup> PM<sub>1</sub> soon after sunrise on 15 January suggests mixing phenomena, whereby elevated concentrations were being mixed down to the surface from the residual layer above. Formaldehyde and organic PM<sub>1</sub> were also elevated during that day but did not display the same temporal increase at sunrise as NO<sub>3</sub><sup>-</sup> PM<sub>1</sub>, perhaps a result of similar abundances between the residual layer and nighttime surface layer concentrations for these compounds. We hypothesize that residual layer NO<sub>3</sub> radical chemistry produces HCHO, NO<sub>3</sub><sup>-</sup> PM<sub>1</sub>, and organic PM<sub>1</sub> at night, and mixing of these secondary products to the surface as the boundary layer expands may explain the elevated daytime concentrations not captured by the MLR model.

From the regression coefficients the MLR model results indicate that residential wood combustion is responsible for the majority of formaldehyde (73%), acetaldehyde (69%), black carbon (55%), and organic PM<sub>1</sub> (100%) abundance, while mobile sources are responsible for most of the CO (83%), benzene (64%), toluene (81%), and C<sub>2</sub>-alkylbenzenes (81%). The percentages were calculated as the fractional contribution of wood smoke and mobile sources to the average concentration of the species above the model offset value C<sub>0</sub>. The C<sub>0</sub> value was similar to the afternoon values of the measured primary pollutants and represents a mixed source component with local contributions from roadway emissions and wood smoke combustion plus advective mass inflow contributions from outside the air shed. Given the low abundances in the afternoon, the PTR-MS measurement precision was not sufficient for the MLR model to separate the afternoon local



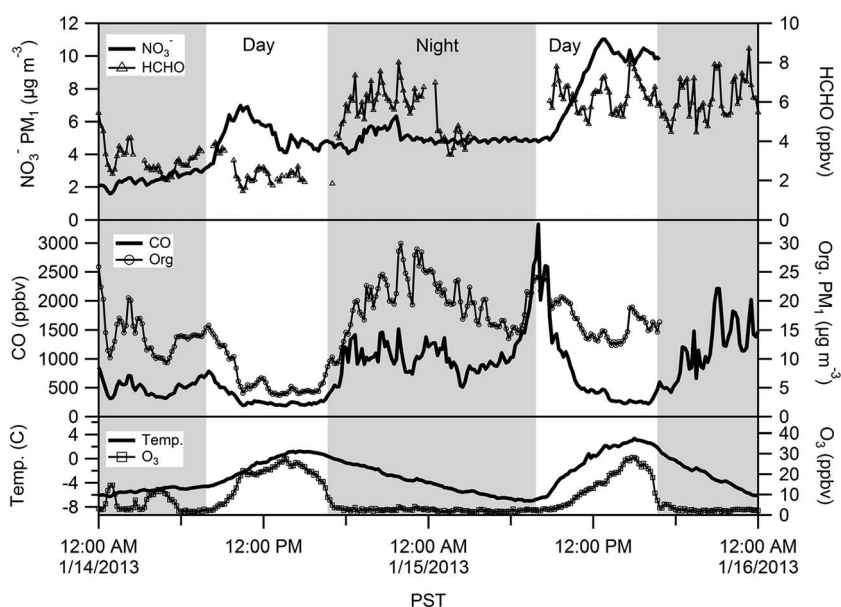
**Figure 3.** Correlations of MLR reproduced pollutant concentrations (y axis) to measured pollutant concentrations (x axis). Units are ppmv for CO; ppbv for formaldehyde, acetaldehyde, benzene, toluene, and C<sub>2</sub>-alkylbenzenes; and  $\mu\text{g m}^{-3}$  for black carbon and organic PM. Open circles indicate the outliers that were identified in the MLR analysis and not included in the regression fit.

**Table 1.** MLR Model Output Factors and  $r^2$  for MLR-Modeled Versus MLR-Measured Correlations Shown in Figure 3a<sup>a</sup>

Compound	Wood Smoke Emission Ratio (mol/mol CH <sub>3</sub> CN)	Mobile Emission Ratio (mmol/mol NO <sub>x</sub> )	C <sub>o</sub> (ppbv)	r <sup>2</sup>
CO	1,135 ± 322.3	12,100 ± 960	161.82 ± 12.63	0.93
HCHO	19 ± 2.1	14.4 ± 5.5	2.25 ± 0.13	0.74
CH <sub>3</sub> CHO	10.6 ± 2.5	9.9 ± 4.5	0.63 ± 0.08	0.80
Benzene	2.8 ± 0.8	10.4 ± 1.6	0.17 ± 0.02	0.82
Toluene	3.2 ± 1.1	28.5 ± 2.6	0.2 ± 0.04	0.87
C <sub>2</sub> -alkylbenzenes	3.4 ± 1.3	33.3 ± 3.1	-0.01 ± 0.05	0.87
Black carbon (g/g, mg/g, $\mu\text{g m}^{-3}$ )	2.7 ± 0.4	5.0 ± 1.3	0.28 ± 0.04	0.81
Organic PM <sub>1</sub> (g/g, mg/g, $\mu\text{g m}^{-3}$ )	64.9 ± 5.0	0.0 ± 14.0	6.87 ± 0.57	0.80

<sup>a</sup>Units for black carbon and organic PM<sub>1</sub> are g/g for the wood smoke emission ratio, mg/g for the mobile source emission ratio, and  $\mu\text{g m}^{-3}$  for C<sub>o</sub>.





**Figure 4.** Time series of O<sub>3</sub>, CO, formaldehyde, organic PM<sub>1</sub>, NO<sub>3</sub><sup>-</sup> PM<sub>1</sub>, and temperature for a clear-sky stagnation event. The onset of the increase in surface air temperature soon after sunrise is coincident with an increase in NO<sub>3</sub><sup>-</sup> and odd oxygen (O<sub>3</sub> + NO<sub>2</sub>), suggesting elevated levels in the residual layer mixing to the surface. Compounds with large primary emission sources, such as CO, typically have lower mixing ratios in the afternoon compared to the evening. The afternoon of the strong stagnation period of 15 January was an exception with high levels of HCHO and organic PM.

source contributions in the air shed from the “regional background” contribution. For some compounds, the model offsets (C<sub>o</sub>) were substantial compared to the average modeled concentration, notably formaldehyde (58%), organic PM<sub>1</sub> (47%), and acetaldehyde (40%). High-offset values were due to high afternoon abundances that may be attributed to secondary sources. Thus, the two-variable primary pollutant source model was not able to explain all the temporal variation observed for these pollutants. The 100% attribution of organic PM<sub>1</sub> obviously reflects limitations in the method for performing source attribution of organic PM<sub>1</sub> since mobile sources are known to emit organic PM<sub>1</sub>. The MLR model is thus likely overestimating the residential wood combustion source because it is larger than the mobile source and thus drives primary organic PM<sub>1</sub> variability. Table 2 summarizes the percentage attributed to each source with associated uncertainty. The uncertainties are the standard deviation of the average percentages calculated from 100 realizations of the regression using block bootstrapping as described above.

These attribution results from MLR model were compared to the 2011 winter emission inventory using the ratio of residential wood combustion percentage contribution to the mobile source contribution. This ratio for both the 2011 winter emission inventory and the MLR model is shown in Table 3. The emission inventory indicates that CO and VOC emissions were dominated by mobile sources, with residential wood combustion to mobile source ratios of 0.11 and 0.26, respectively, and that PM<sub>2.5</sub> was dominated by residential wood combustion, with a ratio of 3.23. The MLR model results generally mirror these conclusions for CO, benzene,

**Table 2.** Average Percentage of Pollutants Attributed to Wood Smoke and Mobile Sources by the Two-Variable MLR Model

Compound	Wood Smoke Percent Contribution	Mobile Source Percent Contribution
CO	17 ± 6	83 ± 4
HCHO	73 ± 9	27 ± 8
CH <sub>3</sub> CHO	69 ± 14	31 ± 6
Benzene	36 ± 9	64 ± 4
Toluene	19 ± 7	81 ± 4
C <sub>2</sub> -alkylbenzenes	19 ± 7	81 ± 5
Black carbon	55 ± 10	45 ± 6
Organic PM <sub>1</sub>	100 ± 8	0 ± 7

**Table 3.** Comparison of the Ratio of Wood Smoke Contribution to Mobile Source Contribution Between the 2011 Winter Emission Inventory and the MLR Model Results<sup>a</sup>

2011 Winter Emission Inventory		MLR Model	
Compound	Wood Smoke/Mobile Source Contribution	Compound	Wood Smoke/Mobile Source Contribution
CO	0.11	CO	0.21
VOCs	0.26	HCHO	2.7
		CH <sub>3</sub> CHO	2.2
		Benzene	0.56
		Toluene	0.23
PM <sub>2.5</sub>	3.2	C <sub>2</sub> -alkylbenzenes	0.24
		Black carbon	1.2
		OPM <sub>1</sub>	∞

<sup>a</sup>The ratios for the 2011 winter emission inventory were molar ratios for CO and VOCs and mass ratios for PM<sub>2.5</sub>. The ratios from the MLR model were on a molar basis for CO, HCHO, CH<sub>3</sub>CHO, benzene, toluene, and C<sub>2</sub>-alkylbenzenes and on a mass basis for black carbon and organic PM<sub>1</sub>.

toluene, C<sub>2</sub>-alkylbenzenes, and organic PM<sub>1</sub>. The ratio for CO suggests that the emission inventory may be underestimating the influence of residential wood combustion by about a factor of 2. Because speciation of VOCs in the emission inventory is sparse, it is difficult to directly compare the wood combustion to mobile source contribution ratio for individual VOCs to the emission inventory. Interestingly, the MLR model results suggest that emissions of the air toxics formaldehyde and acetaldehyde are dominated by residential wood combustion. Aldehydes are known to make up a large portion of the gas phase emissions from residential wood combustion [Schauer et al., 2001]. Benzene, toluene, and C<sub>2</sub>-alkylbenzenes were dominated by mobile source emissions.

The PM<sub>2.5</sub> emission inventory is not speciated, making it difficult to compare the source contribution ratio directly with organic PM<sub>1</sub> and black carbon. The inventory states that residential wood combustion emissions of PM<sub>2.5</sub> are a factor of 3.2 greater than mobile emissions. The MLR model results were consistent with this; the MLR model found the mobile source contribution to organic PM<sub>1</sub> to be negligible compared to wood burning. The black carbon source contribution ratio in the MLR model was evenly split between residential wood burning and mobile sources. This suggests that, in contrast to organic PM<sub>1</sub>, black carbon had a substantial contribution from mobile sources at our study site. This is not necessarily at odds with the emission inventory since black carbon made up a relatively small fraction (~2%) of the overall PM<sub>2.5</sub> mass during the model period.

### 3.4. Comparison of Mobile Source Emission Factors to MOVES

MOVES model results for Yakima County, WA, in the winter season were obtained from WSDOE and compared to results from the chemical mass balance model in Table 4. The MOVES model emissions were reported as a mass per season. For each species of interest in this study, molar emission ratios were calculated using the molecular weight of each compound and reported in units of mmol/mol NO<sub>x</sub>. NO<sub>x</sub> emissions are reported in MOVES as grams of NO<sub>2</sub>, so a molecular weight of 46 was used to convert NO<sub>x</sub> mass emission rates into molar emission rates. The black carbon emission ratio was left in mass units (mg/g NO<sub>x</sub>). MLR emission ratios for benzene and toluene agree well with MOVES, matching almost exactly (within 7%). The

**Table 4.** Comparison of Mobile Source Emission Ratios to NO<sub>x</sub> of the MLR Model Results to MOVES Model Output for Winter Season<sup>a</sup>

Compound	MOVES Emission Ratio to NO <sub>x</sub> (mmol/mol)	MLR Model Emission Ratios to NO <sub>x</sub> (mmol/mol)	MLR/MOVES
CO	16,114	12,099 ± 956	1.33
Formaldehyde	11.4	14.4 ± 5.6	0.79
Acetaldehyde	8.21	9.9 ± 4.5	0.83
Benzene	11.1	10.4 ± 1.6	1.07
Toluene	29.5	28.5 ± 2.6	1.04
C <sub>2</sub> -alkylbenzenes	23.0	33.3 ± 3.1	0.69
Black carbon (mg/g)	16.1	5.0 ± 1.3	3.22

<sup>a</sup>Gas phase pollutant emission ratios are in units of mmol/mol NO<sub>x</sub>, and the black carbon emission ratio is in units of mg/g NO<sub>x</sub>.

formaldehyde and acetaldehyde emission ratios were higher in the MLR model than in moves by 21% and 26%, respectively. However, the MOVES emission ratios are within 1 standard deviation of the MLR emission ratios, meaning that the MLR model did not return results significantly different from MOVES. The C<sub>2</sub>-alkylbenzene emission ratio is estimated about 45% higher by the MLR model than by MOVES. Solvent emissions could have some impact on artificially enhancing this emission ratio, as xylenes are a chemical species listed in the emission inventory documentation for solvents [WSDOE, 2013]. Therefore, it is difficult to say definitively that there are issues with MOVES model estimates of C<sub>2</sub>-alkylbenzene emissions.

The major discrepancies between emission ratios from MOVES and the MLR model occur in the CO and black carbon data. For CO, MOVES predicts an emission ratio that is about 33% greater than what the MLR model returned. One possible reason for this discrepancy is emissions from off-road vehicles and rail traffic, which are large emitters of NO<sub>x</sub> relative to CO. Off-road vehicles, which are mostly heavy-duty diesel engines, are also known to emit significant amounts of black carbon, especially relative to gasoline vehicles [Schauer *et al.*, 1999; Schauer *et al.*, 2002]. It is important to note that the MOVES model was applied on the county level, while this study had a much smaller footprint. This means that black carbon emissions in the urban neighborhood where our study took place may not be representative of on-road black carbon emissions from Yakima County on the whole. While our results suggest that MOVES is overpredicting wintertime on-road black carbon emissions, measurements would need to be performed in more locations to confirm this.

### 3.5. Wood Smoke Emission Factors

While there are many measurements of emission factors developed for wood stove emissions of PM, CO, and VOCs, very few include measurements of acetonitrile. However, one study, by Grieshop *et al.* [2009], made measurements of fresh emissions from a wood stove and reported benzene/CO, toluene/CO, and acetonitrile/CO ratios. The ranges of emission ratios tabulated reflect the range across all wood types used and all burning conditions tested. This included laurel oak and yellow pine wood types and flaming with embers, smoldering and flaming, and smoldering and dying flame-burning conditions [Grieshop *et al.*, 2009]. The CO emission ratio from the MLR model was  $1135 \pm 322$  mol/mol CH<sub>3</sub>CN, which was just below the low end of the range of emission ratios calculated from Grieshop *et al.* [2009], which spanned 1250–10,000 mol/mol CH<sub>3</sub>CN. The observed benzene emission ratio of  $2.8 \pm 0.8$  mol/mol CH<sub>3</sub>CN fits in the low end of the range seen by Grieshop *et al.* [2009], which was 1.0–8.0 mol/mol CH<sub>3</sub>CN. The observed toluene emission ratio of  $3.2 \pm 1.1$  mol/mol CH<sub>3</sub>CN, however, was about 28% higher than the top end of the range from Grieshop *et al.* [2009], which was 0.0–2.5 mol/mol CH<sub>3</sub>CN. Because the MLR model agreed well with observations for CO and toluene ( $r^2 = 0.93$  for CO and  $r^2 = 0.87$  for toluene), this disagreement suggests that wood-burning emissions in Yakima, WA, are somewhat different than the emission profiles reported by Grieshop *et al.* [2009]. This could be due to a variety of factors including stove types, fuel type and fuel seasoning, and burning conditions.

Comparisons were also performed to field observations of organics to acetonitrile [Sarkar *et al.*, 2016] and emission ratios from burning of ponderosa pine [Stockwell *et al.*, 2015] in more recent works. Sarkar *et al.* [2016] presents a field study in the Kathmandu Valley in Nepal during wintertime, which was thought to be heavily influenced by biomass-burning emissions. From their observations of the acetonitrile, benzene, and toluene concentrations  $\pm 1$  standard deviation over the course of their study, ranges of the enhancement ratios of benzene and toluene relative to acetonitrile were calculated. The range for the benzene to acetonitrile enhancement ratio was 1.1–5.5 mol/mol CH<sub>3</sub>CN, and the range for the toluene to acetonitrile enhancement ratio was 0.8–2.7 mol/mol CH<sub>3</sub>CN. The MLR emission ratio for benzene (2.8) was right in the middle of this range, and the emission ratio for toluene (3.2) was about 17% higher than the top of this range. Stockwell *et al.* [2015] performed a detailed set of emission measurements of biomass-burning emissions from different sources. For our study we have chosen to compare their emission ratios for ponderosa pine to the MLR emission ratios, since ponderosa pine is prevalent in the Pacific Northwest and was likely burned in Yakima during our study. Stockwell *et al.* [2015] reported emission ratios of 406–1029 mol CO per mol CH<sub>3</sub>CN, 2.2–4.7 mol benzene to mol CH<sub>3</sub>CN, and 4.2–9.5 mol toluene to mol CH<sub>3</sub>CN. The MLR emission ratio for benzene was within the range reported by Stockwell *et al.* [2015], while the emission ratio for CO was about 10% above the range and the emission ratio for toluene was about 23% below the range. In general, MLR emission ratios to CH<sub>3</sub>CN agreed fairly well with observations from these two more recent papers. Relatively small differences

can likely be explained by difference in fuel types, burning conditions, and types of biomass-burning sources in the case of Sarkar *et al.* [2016].

#### 4. Conclusions

A suite of air pollutants were measured in Yakima, WA, during January 2013 as part of a wintertime air quality study to identify sources of particulate matter. A multiple linear regression (MLR) model was applied to 10 min average data for a 5 day period with large temporal variations in pollutant concentrations. The MLR model attributed pollutant abundance to either residential wood combustion or mobile sources which are the dominant emission sources in the city. Acetonitrile was used as a tracer of residential wood smoke emissions and NO<sub>x</sub> as a tracer of fossil fuel combustion (dominated by vehicle emissions). Results from the MLR model showed that mobile sources were the largest contributors of CO (83%), benzene (64%), toluene (81%), and C<sub>2</sub>-alkylbenzenes (81%), while residential wood combustion was the largest emitter of formaldehyde (73%), acetaldehyde (69%), black carbon (55%), and organic PM<sub>1</sub> (100%). While attribution of all of the organic PM<sub>1</sub> to wood smoke is likely an overestimate, our results suggest that residential wood combustion is not only a major source of PM as expected but also a major source of the air toxics formaldehyde, acetaldehyde, and benzene. Reducing residential wood combustion emissions would thus have a significant multipollutant benefit to air quality. Interestingly, there was a significant component of formaldehyde, acetaldehyde, and organic PM<sub>1</sub> that appeared to be secondary in origin, associated with 2 days during a stagnation event where these compounds were elevated during the morning and afternoon. These elevated periods might be caused by down mixing from the residual layer, implying a nighttime residual layer chemistry source. When comparing MLR model mobile source emission ratios to MOVES 2010b model county-level output we found that the emission ratios to NO<sub>x</sub> agreed very well for benzene and toluene. The emission ratios also agreed within 1 standard deviation for formaldehyde and acetaldehyde. The main differences between MLR results and MOVES model output were in the CO/NO<sub>x</sub> emission ratio, which was a factor of 1.33 higher in the MOVES model output and the black carbon/NO<sub>x</sub> emission ratio, which was a factor of 3 higher in the MOVES model output.

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