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M. A. K. Khalil

Portland State University, aslamk@pdx.edu

R. A. Rasmussen

Oregon Graduate Institute of Science and Technology

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Tracers of Wood Smoke

M.A.K. Khalil

Department of Physics
Portland State University
P.O.Box 751
Portland, Oregon 97207 USA
khalilm@pdx.edu
Tel: 1-503-725-8396; Fax: 1-503-725-8550

R.A. Rasmussen

Department of Environmental Science and Engineering
Oregon Graduate Institute
20000 N.W.Walker Rd
Beaverton, Oregon 97501 USA

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Abstract

Smoke from wood burning is a significant source of air pollution in many parts of the world. When several sources simultaneously cause air pollution it is often difficult to determine how much comes from wood burning. Wood smoke has unique chemical characteristics that can be used as indicators, including elemental composition, particularly potassium and chlorine, the ratios of organic and elemental carbon, and gases such as methyl chloride. This paper deals with formulating and applying the chemical mass balance approach incorporating both gas and aerosol phase tracers to a study carried out at Olympia-Lacey in Washington. In this study, three types of tracers were measured simultaneously and used to estimate wood smoke pollution during Winter, namely elemental composition and organic carbon in the particle phase and methyl chloride in the gas phase. The results from the different tracers are found to be in agreement. The air pollution at the study site was dominated by wood smoke mostly from low temperature combustion (about 80%), with additional but smaller contributions from oil furnaces (15%), automobiles (4%) and occasionally from other nearby sources.

Keywords: methyl chloride, CH_3Cl , receptor model, CMB, regional air pollution

1. Introduction

In many parts of the United States, particularly in the Pacific Northwest, wood burning is a substantial source of air pollution during Winter. When many sources of air pollution are present it is often difficult to determine how much comes from wood burning. Tracers of wood smoke are elements, compounds or gases that come from wood burning in characteristic amounts or ratios. Measurement of these tracers in the environment can be used to quantitatively estimate the amount of air pollution from wood burning. Here we will discuss the major tracers that indicate the presence of wood smoke and how these are used to apportion the observed air pollution among its sources.

Of particular interest is the use of methyl chloride as a novel gaseous tracer of wood smoke. Methyl chloride is a trace gas that comes mostly from natural processes and except for wood burning, it has no known wintertime sources in the Pacific Northwest where we conducted our study. This circumstance makes it a unique indicator of wood smoke providing advantages over other tracers that also come from various local sources such as automobiles and small industry. Carbon is a major constituent of air pollution from combustion processes. The ratios of elemental to organic carbon distinguishes sources such as wood burning, which has a low elemental to organic carbon ratio, and automobiles, which have a high ratio. Carbon analysis also can be used to distinguish between the amount of smoke from hot and cool wood burning. The proportion of cool burning, which produces most of the air pollution, is determined by local practices of using wood stoves and fireplaces. The usual tracers of wood smoke are elemental chlorine and potassium. We will compare the results based on the use of these various and disparate tracers.

We will discuss the general theory and models to represent the sources. We will then apply these ideas to pollution measurements taken at Olympia-Lacey, Washington to calculate the amount of wood smoke present. Finally we will discuss the advantages and limitations of the methods.

2. Theory

Imagine a point source of pollution, such as a chimney. The emission of pollutants, assumed to be fine particles for this discussion, is Q (g/s). The concentration of pollutants, due to this source, at some distant location is:

$$C = Q / \mathcal{D} \quad (1)$$

Where \mathcal{D} is the dilution rate, or the dispersion factor (m^3/s), so that the concentration C is g/m^3 or more traditionally expressed as $\mu\text{g}/\text{m}^3$. Dispersion models are designed to calculate \mathcal{D} based on its dependence on atmospheric characteristics under various environmental conditions, such as wind speed and direction, solar insolation, existence of inversion layers, the location of the sources relative to the point where pollution levels need to be determined and various other variables. Tracer based models provide a means to calculate \mathcal{D} without requiring detailed knowledge of meteorological and environmental conditions. If we measure the emission of an element (Q_T in g/s) at the source as a fraction of the total mass of particles emitted from the source (Q in g/s) per unit time we obtain the emission factor $\mathcal{E} = Q_T/Q$. Assuming that the selected tracer comes only from this source, we note that the concentration of the tracer measured at some distant location (the receptor) is: $C_T = Q_T / \mathcal{D}$ and the concentration of fine particles is as in Eqn 1. The dilution rate is $\mathcal{D} = Q \mathcal{E} / C_T$, which when substituted into Eqn 1 gives:

$$C = C_T / \mathcal{E} \quad (2)$$

We can determine the concentration of fine particles from this source by knowing the emission factor $\mathcal{E} = \mu\text{g}/\text{s}$ of the tracer emitted per $\mu\text{g}/\text{s}$ of fine particles emitted, which is measured at the source, and the concentration of the tracer C_T which is measured at the receptor (here we have used the subscript T to indicate the variable for the tracer). If there are many sources of the same type, wood burning households for example, distributed throughout the region of interest, the

same formula applies. Assuming these to be represented by many point sources ($i=1,\dots,N$) the concentrations of the tracer and the fine particles at the receptor are:

$$C_T = \sum_{i=1}^N Q_{iT} / \mathcal{D}_i \quad \text{and} \quad C = \sum_{i=1}^N Q_i / \mathcal{D}_i \quad (3)$$

Where Q_i is the emission from the i -th source. Since $\mathcal{E} = Q_{iT}/Q_i$ is the same for each source (i), substituting it into Eqn 3 shows the same relationship as for a single source, namely $C = C_T / \mathcal{E}$

In practice there are many different types of sources, all of which may contribute various amounts to the concentrations of a number of tracers. This situation can be expressed as:

$$C_{Ti} = \sum \mathcal{E}_{ij} C_j \quad (4)$$

Where C_{Ti} are the measured concentration of the N tracers at the location of interest (receptor), \mathcal{E}_{ij} are the emission factors representing the emissions of tracer i from source j and C_j are the concentrations of the fine particles that came to the receptor from the j th source type in the region of interest. As in the simple case, the emission factors are measured at the source and the concentrations of the tracers, C_{Ti} are measured at the receptor by collecting aerosol samples. We want to calculate C_j , - the concentration of fine particles that come from source type “ j ”. Casting Eqn (4) in matrix form, we can write the solution vector consisting of C_j as:

$$\underline{C} = \mathcal{E}^{-1} \underline{C}_T \quad (5)$$

This result is for the special case when the number of tracers is the same as the number of expected sources. It is clear that the specific locations of the sources do not have to be known, but we need to know what the sources of air pollution are. Furthermore, we need the emission factors and measurements of the tracer concentrations at the receptor. Moreover, the number of

tracers (N) that are needed must be at least as many as the number of source types (M) that exist in the region of interest. If $N < M$ then the matrix of emission factors \mathcal{E} cannot be inverted to uniquely apportion the pollution among its sources. If there are as many or more tracers than sources, $N \geq M$ it is possible to obtain a source apportionment.

The original idea of such models was to use elements as tracers recognizing that various sources contained one or another element in greater abundance than other sources in the same area (Friedlander, 1977). Lead, for example, would be most abundant in automobile exhaust when lead was still used in gasoline, and sodium or chlorine would be the dominant elements in sea salt aerosols. It is apparent that in theory a tracer can be any compound that is emitted at the same time as the particles from the source, or perhaps even more generally, any attribute of the source that can be measured at the point of emission and the receptor. This generalization extends the tracers that are available for apportioning sources. Specifically, the tracer can be a gas such as CO or H₂ from automobiles and CH₃Cl from wood burning or biomass burning. In such cases, the appropriate emission factor in the matrix \mathcal{E} is $\mu\text{g/s}$ of the gas emitted per $\mu\text{g/s}$ of fine particles emitted and is sometimes expressed in other units more commonly used for concentrations of trace gases such as pptv / μg (pptv=parts per trillion). Another generalization implicit in the theory is that the pollution being apportioned among the various sources need not be fine particles, but could also be a gas. Since gases such as carbon monoxide are also criteria pollutants, we can use this model to determine how much CO is contributed by each source in the region of interest. Such a calculation was done by Khalil and Rasmussen (1988) for Olympia, Washington using part of the same data set that is used in this paper. In that study, molecular hydrogen and methyl chloride were used as tracers of carbon monoxide from wood burning and automobiles. The vector \underline{C} in Eqn (5) consisted of the concentrations of carbon monoxide contributed by various sources and the emission factor matrix consisted of the emissions ratios H₂/CO and CH₃Cl/CO from wood burning and automobiles.

There are several implicit assumptions in the theory which must be met in practical situations. First the dispersion (\mathcal{D}) of the tracer, gas or element, must be exactly the same as that for the

pollutant particles. This is a lesser issue for elements that are embedded in the particles of interest. For gaseous tracers, the assumption is expected to be valid because atmospheric dispersion is by turbulent processes which cause the mixing rate of the gases and fine particles to be about the same. Second, we assume that there is no change in the ratios of the tracer to pollutant by atmospheric production, destruction or deposition along the way between the source and the receptor. And third that the emission factors actually reflect the emissions in the region of interest. This last condition is difficult to achieve because emission factors can vary significantly from one source to another source of the same type even in the same region; from one wood stove to another wood stove for instance. The emission factors for the same source type may also be quite different at one location compared with another.

A quantitative uncertainty analysis is possible by accounting for the known uncertainties in both the emission factors and the measured concentrations at the receptor. Variability in these parameters, if quantified as variances or standard deviations may be propagated as:

$$\sigma_{C_i}^2 = \sum_{j=0}^N (\text{inv } \mathcal{E})_{ij}^2 \sigma_{C_j}^2 + C_j^2 \sigma_{\text{inv } \mathcal{E}_{ij}}^2 \quad (6)$$

Where $\sigma_{\text{inv } \mathcal{E}_{ij}}$ is itself a function of the emission factors \mathcal{E}_{ij} . Here $\text{inv } \mathcal{E}$ is the inverse of the matrix \mathcal{E} and C_i are the concentrations of the aerosol due to the i -th source.

3. The Olympia Study - An Application

The ideas on new tracers and chemical mass balance models were applied to a study we conducted in Olympia, Washington between November of 1985 to March of 1986 with additional measurements during Summer to establish the pollution conditions when wood burning is not present. The main aim of the study was to determine the role of wood burning in wintertime air pollution. The study incorporated an extensive set of simultaneous atmospheric gas phase and particle composition measurements.

3.1 Methods and Measurements

Olympia (capital of Washington state) and Lacey are twin cities located at 47° North latitude and about 122.5° West longitude. The climate is temperate with average Winter temperatures of about 33 °F at night and 47 °F during the day (WRCC). The actual site was located in a large field belonging to a school on College Street and 18th-22nd Avenues. The field was surrounded by houses, many of which used wood for heating as was common practice in the community at the time these experiments were done. Visual observations showed that there was frequent haziness due to wood burning particularly in the evening, but also at other times. The site was considered to be representative of the amount of air pollution that would be typical of residential neighborhoods where wood is a common source of heating. It would also reflect the exposure to residents, although that may be moderated by the fact that the highest wood smoke pollution occurs in the evening and during the nights when most people are indoors.

For the aerosol experiments the sampling equipment consisted of ERT particle collectors that captured fine particles of diameters ≤ 2.5 microns over 6 or 12 hour periods. The fine particulate samples were collected simultaneously on both quartz fiber filters and cellulose acetate filters so that we could measure the trace elemental composition and the organic carbon content. A PM-10 sampler was used to collect particles of diameters ≤ 10 microns integrated over 24 hour periods. For the gas phase experiments air was pumped at a constant rate using a mass flow controller, for 6 hours into a tedlar bag. Then the system switched to a new bag for the next 6 hours and so on. The air sample was transferred to 0.6 L stainless steel containers and sent to the laboratory for analysis. The bags were flushed and used for the next day. An integrating nephelometer was operated continuously to measure light scattering which is usually taken as a proxy for air pollution from atmospheric particles. Light scattering data were recorded hourly, but were averaged over the 6 or 12 hour periods to be comparable to the other measurements. Meteorological data were taken by the Olympia Air Pollution Control Authority.

Chemical analyses were done at three laboratories using standard techniques. The trace

elemental composition was measured using X-Ray Fluorescence Spectroscopy (USEPA, 1999) at NEA Labs; John A. Cooper, President. The elemental and organic carbon analysis was done on the samples collected on quartz filters by Sunset Laboratories, Robert Cary; President. The method used was a thermal oxidation carbon analyzer (Johnson et al. 1981; Huntzicker et al., 1982). The trace gas analyses were done at our laboratory at the Oregon Graduate Center using gas chromatography (Rasmussen and Khalil, 1980; S.A.Edgerton, 1985).

From these measurements we obtained the following data: PM10, TSP, light scattering, PM2.5 on cellulose and quartz filters, elemental composition (Al, Br, Ca, Cl, Cu, Fe, K, Mn, Ni, P, Pb, Si, V, Zn, C, S, Organic carbon - OC and Elemental Carbon - EC) and trace gas concentrations (CHCl_3 , CH_2Cl_2 , CCl_4 , TCE, PCE, CH_3Cl , H_2 , CO , CH_4 , CO_2 , N_2O , F-12, F-11 and F-113). The complete data set consists of the concentrations of these gases and elements at the intervals of either 6 hrs or 12 hrs. The gases were measured integrated over 6-hr intervals, but for the aerosols, 6 hour integrated samples were only collected for about 12 days in mid-December, 1985 and 12-hr periods before and after this period. These data are too voluminous to include here in their entirety. But readers may obtain the full data set from the authors' data archive if needed for further research. In all there are more than 5000 data points. Some 400 filter samples were taken (quartz and cellulose, hence about 200 periods), about 200 gas samples were collected and about 500 light scattering data were recorded over periods that coincide with the integrated measurements of gases and particles. Of the filter samples, about 70 were chosen for trace elemental analysis and about 50 for carbon analysis. The rest of the samples were stored for several years but eventually discarded. The number of samples chosen for detailed analysis was limited by the budget of the project and also the objectives which did not require a more extensive set of measurements. The samples for detailed analysis were chosen to provide data during periods of heavy and low pollution as determined by the frequent light scattering measurements.

The characteristics of the data are summarized in Tables 1 and 2. Table 1 contains the average concentrations of trace gases and elements in the aerosol phase along with the 90% confidence

limits. The averages are divided over low ($0.1 < b_s < 1$), moderate ($1 < b_s < 3$) and heavy ($3 < b_s < 10$) levels of air pollution as determined by the light scattering data. Here b_s indicates the light scattering coefficient in $10^{-4}/\text{m}$. The results show which gases and elements are elevated during air pollution episodes. In Table 2 we show the correlations between the various gas and aerosol phase constituents. These are filtered to contain only those cases when the correlation coefficient is at least 0.5 and is significant at the 99% level or better. Further, the correlation matrix is clustered to put together the tracers that have the highest average correlation with other tracers - these are at the top of the table.

The effects of wood burning are evident from these tables. When the air is polluted, combustion processes and wood burning in particular, are represented by increased levels of K, OC, EC in the particle composition and in CH_3Cl , CO and H_2 in the gas phase (Table 1). As a comparison, the concentrations of methyl chloride at Cape Meares, Oregon which is a nearby clean air marine site, were about 630 pptv during the same time. In the following Summer the concentrations at Olympia were 590 pptv, comparable to clean air at this latitude. The Summer concentrations of methyl chloride in Olympia-Lacey support the idea that other natural or man-made sources do not exist in this area. Since CH_3Cl does not come from combustion processes other than wood burning, it would seem that these patterns reflect the presence of wood smoke.

The correlation matrix (Table 2) further quantifies the inter-relationship of the tracers of wood smoke. Highest correlations are seen among the known tracers of wood smoke such as K, C, OC and CH_3Cl which are also highly correlated with the fine particles and PM10 particle measurements. It is curious that elemental chlorine is not highly correlated with the other tracers, nor does it appear to be highly elevated in polluted air. This may be due to imprecision of measurement and the very low chlorine emission factors under the cool burning such as in wood stoves with closed dampers. In the next section the qualitative patterns seen in these tables are translated into estimates of air pollution from the various sources present and particularly from wood burning using the Chemical Mass Balance approach.

3.2 The Tracers

An ideal tracer has four main characteristics: Uniqueness - that it comes from only one type of source; Constancy - that operational and environmental conditions at the source do not effect the emission factor; Inertness - that the tracer is not lost between the source and the receptor any more or less than the pollutant of interest; And high precision of measurement so that we can measure its concentrations exactly. No actual tracer for any source can satisfy all these characteristics. Some deficiencies can be overcome while others can make the calculations highly uncertain.

For wood burning the emissions that could be used as tracers in a chemical mass balance model tend to have large variability depending on the conditions under which the wood is being burned, especially the temperature of the combustion. Methyl chloride is a useful tracer of wood burning because its emission factor is less affected by combustion temperature, and it has no other sources in most areas where wood burning is a source of air pollution (Khalil et al. 1983; Edgerton, 1985). The known sources of methyl chloride are mostly natural including the oceans, fungal activity in soils and rotting of wood mostly in the tropics, and a few other minor sources. Long-term global measurements show that some 85% of the world wide annual emissions occur in the tropics (Khalil and Rasmussen, 1999). In the middle latitudes such as in the Pacific Northwest region of the United States, where our studies were conducted, we have not been able to identify any sources of methyl chloride other than biomass burning and specifically wood burning in the Winters. While methyl chloride may be a unique tracer of wood burning in the region of our experiments, there is a sizable background concentration of about 600 pptv. The excess created by wood burning is relatively small (10%-20%). This small residual, along with the lack of high precision of measurement cause uncertainties in estimating wood burning pollution using methyl chloride.

The temperature of the burn and the type of wood that is being burned also lead to the variability of the emission factor. The most extensive data are from a number of field experiments done by

Dr. Darold Ward of the U.S. Forest Service (retired). Between 1982 and 1986 he collected air samples in tedlar bags from various forest slash burns. These were analyzed in our laboratory at the Oregon Graduate Center using the same methods as in the Olympia-Lacey study discussed here. While the emission factor of methyl chloride and other tracers varied widely in these studies we have pooled the data to look at the emission factor of the composite effect of burning various types of local forest woods. The temperature was not directly measured, but records were kept of when the slash pile was flaming or smoldering and various stages in between. We propose that the dimensionless ratio of carbon dioxide to carbon monoxide would be a very good proxy for the temperature of combustion. A high ratio means a hot flaming condition and a low ratio means a high emission of carbon monoxide which is indicative of incomplete or cooler combustion. Indeed the cases of flaming and smoldering combustion matched with the high and low ratios of carbon dioxide to carbon monoxide respectively. In Figure 1 we show the results of these studies conducted in Oregon and Washington that quantify the effect of temperature on the emission factor. In this figure the ratios are given in pptv $\text{CH}_3\text{Cl}/(\text{micrograms}/\text{m}^3 \text{ particles})$ and dimensionless units for the elemental tracers. In addition to the field data from the forest slash burns, we have also included data from laboratory measurements on wood stoves in the Portland area under hot and cool burning conditions represented by open and closed damper systems (Edgerton, 1985; Rau, 1986).

The results show that methyl chloride composite emission factor does not change much with the temperature of the burn, while the emissions of the elemental tracers can change by a factor of 10 or so. Moreover, the emission factors of the elemental tracers are very small for low combustion temperatures, hence making it difficult to measure the concentrations if the pollution from wood burning is dominated by cool burning conditions, as we will show was the case in the Olympia-Lacey study. Methyl chloride emissions on the other hand are abundant under cool burning conditions.

Although potassium or chlorine are used as tracers of wood burning, elemental and organic carbon are also excellent tracers. Combustion process produce an aerosol that is mostly carbon,

but the ratio of elemental to organic carbon (EC/OC) is an indicator of the temperature of the burn. High temperature combustion is likely to produce mostly elemental carbon and low temperature combustion would produce large amounts of organic carbon. Thus the ratio EC/OC can distinguish between pollution from cool burning of wood and hot, flaming combustion or the emissions from internal combustion engines including automobiles. The measured emission factors used in our work are given in Table 3.

3.3 Wood Burning Pollution in Olympia-Lacey Experiments

Based on the preceding discussion we calculated the amount of air pollution that can be attributed to various sources in the region of our experiments using the chemical mass balance methods. These methods are a bridge between the qualitative knowledge of sources and desired estimates of the contributions from each source. We start by taking an inventory of the known major sources. For the Winter season we took the sources in Olympia-Lacey to be wood burning, automobiles and oil furnaces. We also took source samples at a plywood factory that had veneer dryers and hogged fuel burners, neither of which was a strong source of methyl chloride or the other tracers of wood burning. If there were additional sources that contributed to the observed air pollution they escaped our notice.

As “the standard” we used U.S.EPA’s Chemical Mass Balance Model, Version 6 (Watson, 1979; Watson, 1984; USEPA, 1987). This model was used with two different source emission profiles - the first was the standard source profile that is included in the EPA source library at the time of our experiment, designated M-EPA for future reference (Core et al., 1984) and the second included the emission factors for organic and elemental carbon for hot and cold wood burning and automobiles as reported by Rau (1986), designated M-EPA/C (indicating the inclusion of elemental and organic carbon by the “C”). Next we used four “custom” models using a combination of gases and elemental tracers for the known sources. The custom models are very small compared with the standard model and consist of two or three components in the form of

Eqn 5. The simplest are two 2-component models that estimate the contributions of wood burning and automobiles. One uses aerosol tracers Pb and OC (designated M-2) and the other uses only gas tracers CH₃Cl and CO (M-2Gas). The two component models are extraordinary in their simplicity. Based on Eqn 5, for M-2 the estimates of pollution from wood burning and automobiles are written as:

$$C_{\text{auto}} = C_{\text{Pb}} / \mathcal{E}_{\text{Pb/Auto}} \quad (6a)$$

$$C_{\text{WB}} = (C_{\text{OC}} - \mathcal{E}_{\text{OC/Auto}} / \mathcal{E}_{\text{Pb/Auto}} C_{\text{Pb}}) / \mathcal{E}_{\text{OC/WB}} \quad (6b)$$

and for M-2Gas the equations are:

$$C_{\text{auto}} = (\Delta[\text{CO}] - \mathcal{E}_{\text{CO/WB}} / \mathcal{E}_{\text{CH}_3\text{Cl/WB}} \Delta[\text{CH}_3\text{Cl}]) / \mathcal{E}_{\text{CO/Auto}} \quad (7a)$$

$$C_{\text{WB}} = [\text{CH}_3\text{Cl}] / \mathcal{E}_{\text{CH}_3\text{Cl/WB}} \quad (7b)$$

Here $\mathcal{E}_{x/y}$ is the emission factor of tracer x from source y, Δ is the excess over background concentrations and WB stands for wood burning.

The remaining two models have four components consisting of K, OC, Pb and S (designated as M-4) and the other is a mixed gas and elemental composition model with CH₃Cl, K, Pb and S (designated as M-4Mixed). These models resolve hot and cool wood burning, automobiles and oil furnace pollution. In the gaseous tracer 2-component model (M2-Gas), the amount of wood smoke in the measured samples is given by Eqn 7a, which requires knowledge only of the CH₃Cl concentration and the emission factor ($\mathcal{E}_{\text{CH}_3\text{Cl/WB}}$). Once we have calculated the concentration of wood smoke, we can figure out how much CO would come with it from wood burning since we have the emission factor of CO/Particles from wood burning ($\mathcal{E}_{\text{CO/WB}}$). Next, by subtracting the background CO and the amount that came from wood burning, we are left with a residual that we attribute to automobiles. Knowing the emission factor for CO/Particles from automobiles ($\mathcal{E}_{\text{CO/Auto}}$), we can now estimate the amount of fine particles that are contributed by automobiles. This process is illustrated in Eqns 7a-b. In this case however, we are assuming that the residual

CO, not accounted by wood burning, can all be allocated to automobiles. This may not be valid in more complex environments and when photochemical production of CO is present. It may only be a rough approximation for the Olympia-Lacey Study.

In the standard model all the elemental data and the measured concentrations of organic and elemental carbon were entered. When organic and elemental carbon data were available, we were able to distinguish between the contribution from hot wood burning and cool wood burning. These were added to arrive at a total that is used for the comparisons of results with methods that did not distinguish between the two. This did not have much effect since most of the observed pollution fitted cool burning characteristics.

The results are shown in Figures 2 a-d. In these figures we have plotted the estimates of the contribution of wood burning, oil furnaces, automobiles and hot wood burning. In these calculations we have used a the same set of sources for each day when there were sufficient data and the same emission factor is used throughout. On rare occasions we found small contributions from the plywood factory of 1-10 $\mu\text{g}/\text{m}^3$ as determined by the CMB model using the source profiles from the specific nearby factory. A few calculations gave invalid results because the calculated total fine particle concentrations exceeded the measured concentrations by more than 10% - such cases were discarded since to resolve these would require information that no longer exists.

Quantitative comparison between the outputs of the various models were done by calculating the correlation coefficients between the predictions. We will look at a selected set of correlation coefficients to discuss the level of agreement between the various calculations. The comparisons are with the standard EPA model using elemental and organic tracers, which we consider to be the most detailed calculation for wood burning. To describe the results we use a the symbol $r(\text{Model 1, Model 2} \mid \text{Source Type})$. As an example $r(\text{M-EPA/C, M-EPA} \mid \text{Cool WB})$, should be read as the correlation coefficient between the standard EPA model with carbon composition tracers (M-EPA/C) compared with the standard EPA model with the standard source library of

wood burning tracers, for cool wood burning calculations.

For cool wood burning the correlations are $r(\text{M-EPA/C, M-EPA|Cool WB}) = 0.893$, $r(\text{M-EPA/C, M-2|Cool WB}) = 0.998$, $r(\text{M-EPA/C, M-2Gas|Cool WB}) = 0.571$, $r(\text{M-EPA/C, M-4|Cool WB}) = 0.999$ and $r(\text{M-EPA/C, M-4Mixed|Cool WB}) = 0.623$. These results demonstrate that when elemental tracers are used the agreement between the calculations is very high even when small models are used. The agreement is less when methyl chloride is used instead of the elemental tracers. Nonetheless the correlations are still good and may be improved if a few outliers were excluded as can be seen from Fig 2. It happened that during the times when the highest levels of wood smoke were calculated the methyl chloride sampling system had not yet been installed and later we missed some pollution episodes when it stopped working for a while. This and the fact that there is variability in the measured excess methyl chloride since a sizable background has to be subtracted from the ambient measurement, may explain why the correlations are somewhat lower. For hot wood burning $r(\text{M-EPA/C, M-4|Hot WB}) = 0.857$ and $r(\text{M-EPA/C, M-4Mixed|Hot WB}) = 0.753$. For oil furnaces, $r(\text{M-EPA/C, M-EPA|Oil Furnaces}) = 0.99$, $r(\text{M-EPA/C, M-4|Oil Furnaces}) = 0.993$ and $r(\text{M-EPA/C, M-4Mixed|Oil Furnaces}) = 0.992$. For these sources (hot wood burning and oil furnaces) the agreements between the applicable models is very close. For the automobile contribution the agreements are much weaker than the other sources with $r(\text{M-EPA/C, M-EPA|Auto}) = 0.583$, $r(\text{M-EPA/C, M-2|Auto}) = 0.558$, $r(\text{M-EPA/C, M-2Gas|Auto}) = 0$, $r(\text{M-EPA/C, M-4|Auto}) = 0.595$ and $r(\text{M-EPA/C, M-4Mixed|Auto}) = 0.594$. As seen in Fig 2 the various models do not agree well on the estimated contribution of automobiles to air pollution in our experiments. The worst is the use of CO in the 2-component gaseous tracer model. As mentioned earlier, the assumptions of this model are perhaps not valid for our situation, yet it is noteworthy that the average contribution predicted by this small model is in agreement with the results of the other models.

The results show that the various models perform similarly and all are in agreement for the major sources isolated in this study. As the calculated concentrations of wood burning pollution become large, the disagreement between methods increases (Fig 2a). After wood burning, oil

furnaces are seen as the next highest contributors to the observed air pollution. Here the simple models are in very close agreement with the standard EPA CMB model (Fig 2b). The contribution of automobiles to particulate pollution is small. Although there is considerable scatter in the results of the different models, all show only 2-6 micrograms/cm³ from automobiles. These estimates do not take into account any secondary formation of aerosols which is also not expected to be large because the measurements were taken during Winter (Fig2c). In the trace gas measurements, the lack of elevated nitrous oxide is also consistent with small automotive sources. Nitrous oxide is emitted more by cars with catalytic converters which may not have been as prevalent at the time of the study as they are now. It is noteworthy that estimates of pollution from hot burning are also of the order of a few micrograms per cubic centimeter (Fig 2d). We would expect this since the emissions experiments show that there is little smoke generated under hot flaming conditions. Moreover, such hot conditions do not last long as most wood heating requires controlling the burning rate to get slow release of heat. A load may last the entire night as the dampers on wood stoves are closed to create cooler burning conditions. Therefore, the majority of the air pollution observed in our experiments came from cool wood burning.

For the case study at Olympia-Lacey, we can summarize the results by calculating the weekly contributions to air pollution from the four sources we have discussed: Cool wood burning, oil furnaces, hot wood burning and automobiles. The cool wood burning results are the difference between the estimated pollution from all wood burning and hot wood burning (Fig 3). These sources explain 80%-100% of the observed concentrations of fine particles with about 80% due to wood burning, about 15% due to oil furnaces and 4% from automobiles.

4. Conclusions

Wood smoke pollution is confined to only some parts of the United States and then only to Winters, but it may be more prevalent in other parts of the world. Although less studied,

pollution from biomass burning including forest fires or agricultural activities such as grass field burning that is prevalent in Oregon, may contribute to air pollution in U.S. cities at other times of the year. This pollution from biomass burning in general and wood burning in particular has unique characteristics that can be used to determine how much of it comes from this source. The commonly used elemental tracers such as potassium and chlorine have large emission variability and very low emission factors that may lead to uncertain estimates. Tracers such as the ratio of organic to elemental carbon or the excess of methyl chloride, offer alternative approaches to evaluating the impact of wood burning on air pollution.

There have been a few studies on the use of the novel tracers and we have discussed one of these here. The results are compatible with the standard methods and likely to be more accurate. Our emphasis has been on methyl chloride as a tracer of wood smoke, but other gases can also be used. For methyl chloride the major advantages are that nearly real time measurements of wood smoke pollution can be taken because sampling times can be as short as 5 minutes (Edgerton, 1985, Ward et al., 1982). The samplers are portable and can be carried anywhere with ease requiring a small battery for operation. It is also easy to calculate the resulting air pollution from wood burning since there are very few other sources of methyl chloride that would interfere with the signal. These are significant advantages, but at the same time there are difficulties. One major issue is the background concentration which has to be subtracted to determine the excess that can be attributed to wood burning. The background and its natural variability are very well characterized for clean marine air, but for specific urban areas the appropriate background to subtract is not easily determined and may be affected by air circulation patterns. The variability of the emission factor for different types of wood and even the effect of combustion temperature have not been adequately determined.

Because there are no other significant known sources of methyl chloride in urban areas, calculations of wood smoke pollution can be greatly simplified relative to elemental tracers that require the larger Chemical Mass Balance Models through which the source has to be resolved by successively subtracting parts of the tracer concentrations attributed to other sources. In the

present study we were dealing with an environment which had a few major sources during the Winter. Under these circumstances very small CMB models can be implemented that produce results that are comparable with the standard models. This is important because the small models are transparent, the assumptions being made are clearly known and uncertainties in all aspects can be easily propagated, isolated and studied and thus used to improve future measurement strategies. Moreover the ability to verify the results of the standard models improves the understanding of the environmental science of the regions being studied.

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Figure Captions:

Figure 1. The emission factors for tracers of wood smoke in forest slash burns in the Pacific Northwest region of the United States. The temperature of combustion can affect the chemical composition of the wood smoke. We see here that elements such as K and Cl and methyl chloride can be greatly enriched in smoke from hot, flaming combustion of wood and biomass. Although temperature was not directly the ratio of CO₂ to CO is used as a proxy. In the side bar key, fp = fire places.

Figure 2. Calculated amounts of air pollution from wood burning, oil furnaces and automobiles in Olympia-Lacey, Washington during the winter of 1985-1986. Several methods were used, both traditional and new as discussed in the text. The different tracers yield similar results. In this case low temperature wood burning is the major source of air pollution with lesser contributions from the other identified sources, namely, oil furnaces and automobiles. Units are $\mu\text{g}/\text{m}^3$ for both axes. The standard model is on the horizontal axis. It uses an EPA Chemical Mass Balance Model with data on organic and elemental carbon emissions (M-EPA/C). The other models, described in the text, are: M-EPA which is the EPA model with standard source profiles. M-2 has only two components and sources. It uses only Pb and Organic Carbon (OC) as tracers. M-2Gas uses only gaseous tracers CH₃Cl and CO. M-4 consists of four components and tracers K, OC, Pb and S and M-4 Mixed uses both gas and elemental composition as tracers - CH₃Cl, K, Pb and S.

Figure 3. A weekly average estimate of air pollution from various sources in the Olympia-Lacey Study during the Winter of 1985-1986.

References

- Core, J.E., J.J.Shah and J.A.Cooper (1984) Receptor Model Source Composition Library (U.S.EPA, RTP NC, 1984)
- Edgerton, S.A. (1985) Gaseous Tracers in Receptor Modeling: Methyl Chloride Emission from Wood Combustion (Ph.D Dissertation, Oregon Graduate Center, Beaverton, OR.)
- Friedlander, S.K. (1977). Smoke, Dust and Haze (Wiley, N.Y.).
- Khalil, M.A.K.; S.A.Edgerton and R.A.Rasmussen (1983), A gaseous tracer model for air pollution from residential woodburning. *Environmental Science and Technology* 17, 555-559.
- Khalil, M.A.K and R.A.Rasmussen (1988). Carbon monoxide in an urban environment: Application of a receptor model for source apportionment. *JAPCA*, 38, 901-906.
- Khalil, M.A.K. and R.A. Rasmussen (1999). Atmospheric methyl chloride. *Atmospheric Environment* 33, 1305-1321.
- Johnson, R.L., J.J.Shah, R.A.Cary and J.J.Huntzicker (1981). An automated thermo-optical method for the analysis of carbonaceous aerosol. In *Atmospheric Aerosol Source/Air Quality Relationships*. Macias, E.S.and P.K.Hopke (Eds). (ACS Symposium Series No. 167). 223-283.
- Huntzicker, J.J., Johnson, R.L., J.J.Shah and R.L.Cary (1982). Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method. In *Particulate carbon: Atmospheric Life Cycle*. Wolff, G.T. and A. Klimish (Eds) (Plenum Press, N.Y) 79-88.
- Rasmussen, R.A. and M.A.K.Khalil (1980). Atmospheric halocarbons: Measurements and analyses of selected trace gases. Proceedings of the NATO advanced study institute on atmospheric ozone: Its variation and human influences. A.C. Aikin Editor (FAA, Washington D.C., Document # FAA-EE-80-20)
- Rau, J.R. (1986) Residential Wood Combustion Aerosol Characterization as a Function of Size and Source Apportionment Using Chemical Mass Balance Modeling (Ph.D Dissertation, Oregon Graduate Center, Beaverton OR.).
- US EPA (1987). Receptor model Technical Series, Volume III (Revised) . CMB User's Manual (Version 6.0). EPA-450/4-83-014R, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- US EPA (1999). Compendium Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy. EPA/625/R-96/010a, Center for

Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.

Ward, D.E., C.C. Hardy, R.D. Ottmar, and D.V. Sandberg (1982). A sampling system for measuring emissions from west coast prescribed fires. In: Proceedings of the Air Pollution Control Association, Pacific Northwest International Section, Vancouver, B.C., Nov. 15-17, 1982.

Watson, J.G. (1979) Chemical Element Balance Receptor Model Methodology for Assessing the Source of Fine and Total Suspended Particulate Matter in Portland, Oregon. (Ph.D Dissertation, Oregon Graduate Center, Beaverton OR.).

Watson, J.G. (1984). Overview of receptor model principles. JAPCA 34, 62-623.

WRCC (Western Regional Climate Center), Olympia WSO AP 456114, Monthly Tabular Data 1961-1990, www.wrcc.dri.edu.

Table 1. Concentrations of trace gases and trace elements in the aerosols at Olympia-Lacey, Washington During the Winter of 1985-1986. The \pm values are the 90% confidence limits of the means.

Bscatt	Pollution level								
	Low			Moderate			High		
	0.1 - 1			1 - 3			3 - 10		
PM10	40.2	\pm	4.1	56.9	\pm	4.9	117.0	\pm	11.0
TSP	49.1	\pm	7.7	74.2	\pm	9.5	143.3	\pm	22.3
Cellulose	17.4	\pm	2.5	41.7	\pm	3.5	91.3	\pm	8.5
Quartz	16.0	\pm	2.6	34.2	\pm	4.2	82.1	\pm	10.8
CHCl ₃	66.5	\pm	13.3	115.3	\pm	12.3	130.0	\pm	22.1
CH ₃ CCl ₃	303.9	\pm	44.6	414.1	\pm	27.4	532.2	\pm	65.9
CCl ₄	133.1	\pm	1.0	132.0	\pm	1.0	131.5	\pm	2.0
TCE	75.4	\pm	15.7	87.3	\pm	15.3	78.7	\pm	20.2
PCE	228.3	\pm	52.7	541.7	\pm	100.5	657.6	\pm	120.2
CH ₃ Cl	580.0	\pm	4.7	634.7	\pm	4.9	740.9	\pm	14.1
H ₂	691.5	\pm	43.1	817.8	\pm	47.3	890.2	\pm	87.2
CO	631.4	\pm	103.4	1030	\pm	118.2	1463	\pm	269.6
CH ₄	1819	\pm	24.7	1877	\pm	46.0	1919	\pm	49.8
CO ₂	368.3	\pm	2.9	377.1	\pm	9.2	382.9	\pm	8.2
N ₂ O	310.4	\pm	1.5	309.4	\pm	1.1	308.6	\pm	5.1
F-12	562.9	\pm	69.9	593.3	\pm	88.5	640.7	\pm	152.9
F-11	264.0	\pm	6.4	578.0	\pm	249.2	278.9	\pm	10.4
F-113	172.3	\pm	119.1	319.1	\pm	69.5	289.4	\pm	115.7
Al	0.065	\pm	0.012	0.101	\pm	0.015	0.113	\pm	0.013
Br	0.006	\pm	0.002	0.020	\pm	0.004	0.032	\pm	0.005
Ca	0.019	\pm	0.003	0.030	\pm	0.007	0.032	\pm	0.004
Cl	0.136	\pm	0.042	0.129	\pm	0.068	0.197	\pm	0.043
Cu	0.004	\pm	0.001	0.006	\pm	0.001	0.007	\pm	0.001
Fe	0.016	\pm	0.004	0.040	\pm	0.011	0.047	\pm	0.008
K	0.098	\pm	0.033	0.299	\pm	0.035	0.655	\pm	0.095
Mn	0.004	\pm	0.001	0.006	\pm	0.001	0.007	\pm	0.001
P	0.029	\pm	0.005	0.042	\pm	0.009	0.048	\pm	0.007
Pb	0.018	\pm	0.006	0.051	\pm	0.010	0.091	\pm	0.015
Si	0.090	\pm	0.026	0.164	\pm	0.041	0.196	\pm	0.034
Ti	0.004	\pm	0.000	0.006	\pm	0.002	0.005	\pm	0.001
V	0.009	\pm	0.011	0.006	\pm	0.001	0.005	\pm	0.001
Zn	0.068	\pm	0.029	0.086	\pm	0.024	0.096	\pm	0.017
C	11.7	\pm	5.6	23.5	\pm	5.2	59.7	\pm	10.1
S	0.4	\pm	0.1	1.3	\pm	0.3	1.6	\pm	0.2
OC	10.9	\pm	5.2	21.4	\pm	4.9	55.7	\pm	9.3
EC	0.8	\pm	0.4	2.1	\pm	0.4	4.1	\pm	1.3

Aerosol constituents are in micrograms per cubic meter, CO₂ is in ppmv, CH₄, CO and N₂O are in ppbv and the rest of the gases are in pptv.

Table 2. Correlations between the various gas and aerosol phase constituents, filtered to show only those cases where the correlation coefficient (r) is at least 0.5 and is significant at the 99% level or better.

	K	C	CELLULOSE	OC	EC	QUARTZ	PB	BR	BSCATT	CH ₃ Cl	PM10	CH ₄	H ₂	PCE	S	CO ₂	Mn	CO	CH ₃ CCl ₃	
K	1.00	0.95	0.96	0.95	0.68	0.93	0.72	0.79	0.84	0.79	0.80	0.74	0.66	0.75	0.58	0.62				
C	0.95	1.00	0.97	1.00	0.70	0.98	0.61	0.66	0.81	0.53	0.81	0.63	0.69			0.61				
cellulose	0.96	0.97	1.00	0.97	0.65	0.94	0.62	0.70	0.81	0.75	0.78		0.57		0.57				0.56	
OC	0.95	1.00	0.97	1.00	0.64	0.98	0.60	0.64	0.80	0.53	0.81	0.62	0.69			0.61				
EC	0.68	0.70	0.65	0.64	1.00	0.89	0.54	0.63	0.58	0.52	0.66	0.64	0.64	0.55		0.59				
QUARTZ	0.93	0.98	0.94	0.98	0.89	1.00	0.60	0.58	0.77	0.62	0.80								0.50	
PB	0.72	0.61	0.62	0.60	0.54	0.60	1.00	0.90	0.75	0.52				0.83			0.61		0.63	
BR	0.79	0.66	0.70	0.64	0.63	0.58	0.90	1.00	0.75					0.88	0.65				0.51	
BSCATT	0.84	0.81	0.81	0.80	0.58	0.77	0.75	0.75	1.00	0.93	0.71									
CH ₃ Cl	0.79	0.53	0.75	0.53	0.52	0.62	0.52		0.93	1.00	0.55						0.53			
PM10	0.80	0.81	0.78	0.81	0.66	0.80			0.71	0.55	1.00									
CH ₄	0.74	0.63		0.62	0.64							1.00	0.63		0.61	0.90			0.65	
H ₂	0.66	0.69	0.57	0.69	0.64							0.63	1.00			0.73			0.79	
PCE	0.75				0.55		0.83	0.88							1.00	0.60		0.78		0.56
S	0.58		0.57					0.65				0.61		0.60	1.00					
CO ₂	0.62	0.61		0.61	0.59							0.90	0.73			1.00			0.72	
MN							0.61			0.53				0.78			1.00		0.70	
CO			0.56			0.50						0.65	0.79			0.72		1.00		
CH ₃ CCl ₃							0.63	0.51						0.56			0.70		1.00	

Note: Correlations were also calculated for Al, Si, V, Fe, F-11, P, F-113, TCE, CHCl₃, Zn, Ca, As, F-12, Ti, Cu, N₂O, Cl, Ni, and CCl₄ with each other and the gases and elements shown in this table. The correlation of Al with P was 0.71; S with P was 0.68; Fe with Mn was 0.65. Correlations greater than 0.60 and less than 0.65: Al and Si; Pb and Si; Al and S; Ni and V; F-113 and Zn; CH₃CCl₃ and TCE. Correlations greater than 0.50 and less than 0.60: F-11 with C, OC, and TCE; Br with Si and As; CH₃Cl with Ni; Fe with Ca and Al; CHCl₃ with S and V; Si and Mn; F-113 and V; Ni is negatively correlated with C and OC; CCl₄ and Br are negatively correlated. All other pairs were not significant.

Table 3: Emission factors of selected tracers used in this study.

Tracer	Source			Oil Furnaces
	Wood Burning		Automobiles	
	Hot	Cool		
Pb	0.00075	0.0	0.046	0.00132
OC	0.175	0.535	0.16	0.14
EC	0.25	0.04		
K	0.1025	0.001625	0.0027	0.00016
S	0.1825	0.0007	0.042	0.12
CH ₃ Cl	1.67	0.6	0.0	0.0
CO		30	152	

Emission factors are dimensionless in $\mu\text{g m}^{-3}$ of tracer / $\mu\text{g m}^{-3}$ fine particles. For CH₃Cl the emission factor is in pptv/ $\mu\text{g m}^{-3}$ and for CO it is in ppbv/ $\mu\text{g m}^{-3}$.











