GASEOUS TRACERS IN RECEPTOR MODELING:
METHYL CHLORIDE EMISSION FROM WOOD COMBUSTION

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Dedicated to Erin and to Darrell, with love.

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ABSTRACT

GASEOUS TRACERS IN RECEPTOR MODELING:
Methyl Chloride Emission from Wood Combustion

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The model and the statistical and experimental techniques for using gaseous species to trace sources of particulate air pollution are developed. The model is implemented in a simple environment and the results are compared with those obtained from the concurrent application of other models. In particular, measurements of elevated concentrations of the gas methyl chloride, CH_3Cl, in the Portland, Oregon area are used to quantify the contribution of residential wood combustion to fine particulate pollution.

The method requires accurate measurements of the gas to aerosol ratios in the source emissions and knowledge of all sources contributing to the ambient concentrations of the gases. The source emission factors for the ratio of CH_3Cl to aerosol from woodburning are presented for different types of wood and burn conditions along with measurements of the background concentrations of CH_3Cl at both an urban and a remote global site.

The advantages of using gaseous tracers to apportion the sources of particulate pollution include: (1) the continuous in situ monitoring which provides real time estimates of the source contributions and therefore of personal exposures, and (2) the inclusion of a gaseous species, such as CH_3Cl for woodburning, in the multicomponent Chemical Mass Balance (CMB) receptor model can help distinguish source contributions among sources with similar elemental characterizations.

The results of using CH_3Cl to estimate the contribution of woodburning to particulate air pollution show that the evening, wintertime averaged concentrations of fine particles from woodburning ranges from 10 $\mu g/m^3$ in a hilly, windy neighborhood to 50-73 $\mu g/m^3$ in neighborhoods on low terrain subject to poor meteorological dispersion. Woodburning emissions may be a major cause of the nonattainment of air quality standards in many urban areas. The uncertainty of the woodburning contribution using CH_3Cl measurementts is generally less than 30%.

The implications of applying the CH_3Cl model suggest an important health risk from woodsmoke may be that of acute exposure to more susceptible members of the population. A greater health concern exists over exposure to woodsmoke in developing countries where cooking with biomass fuels in rooms with little ventilation is common.

INTRODUCTION

"We can't win."
"We are sure to lose."
"We can't get out of the game."

The three laws of thermodynamics
paraphrased by Garrett Hardin

"If it offends the moral sense to be born into some cosmic Las Vegas with unbreakable house rules and with no chance of escape, think instead how wonderful it is that we have survived as a species in a world of one-arm bandits and still have a chance to take stock and plan our future tactics."

J.E. Lovelock discussing these
laws in Gaia

The earth's atmosphere is a dynamic component of the biosphere which sustains human life. We seek to better understand its origin, composition, evolution and the potential influence of life in altering its chemical and radiative properties. Our concern is focused not only on local air pollution but also on the possible perturbation of global atmospheric processes caused by human activities. By studying the cycles of atmospheric constituents we can ascertain bits and pieces of the larger dynamic process which is responsible for maintaining the balance by which the biosphere is able to exist as a life supporting system. This balance may indeed be robust, as suggested by the Gaian Hypothesis which postulates that the Earth's biosphere "is a self-regulating entity with the capacity to keep our planet healthy by controlling the chemical and physical environment" (Lovelock, 1979). However even if life as a singular entity possesses the code to ensure its own survival, individual species have become extinct. We must wonder if Gaia will uphold our anthropocentric notion of the sanctity of the human species. Meanwhile as we ponder these somewhat philosophical ideas, we might probe into the mechanics of those biospheric processes on which our survival depends. Perturbations in the cycles of the oceans and the atmosphere may alert us to possible future imbalances which may portend changes in the earth's ability to support the style of life to which we are accustomed.

One aspect of the study of atmospheric cycles is the knowledge of the sources, sinks and transport of atmospheric constituents. In this dissertation I will study the perturbations in the cycles of gaseous species in the atmosphere to identify the sources of those species and the suspended particulate matter which accompanies them. In particular, concentrations of the gas methyl chloride, CH_3Cl, will be used to apportion the contribution of residential wood burning to fine particle concentrations in an urban environment.

Wood has been called the fuel of civilization. Its earliest use on earth may have been by hunters to flush game from cover by setting brush fires. It was used as fuel for cooking for hundreds of thousands of years, to smelt copper and lead 7000 years ago and it has enhanced the survival of human beings over the ages (Smith, 1981;

Tillman, 1978; Saver, 1969; Harris, 1975). That the wood fires that sustained our ancestors for many thousands of years should constitute a health hazard for us now may seem incredible. Yet with the rapid increase of human population that our world is now experiencing and with a growth rate of energy consumption several times that of the population growth rate in developing countries, the future use of wood as a fuel is increasing at a rate never before experienced in the history of mankind. Although there is a limit to biomass reserves, the reutilization of forest waste and the development of tree farms for use in the production of energy could cause the amount of biomass burned annually to increase dramatically. Rural household energy demand in developing countries can account for 50 to 75% of the national energy demand of these countries and is met mostly by fuelwood (O'Keefe et al., 1984). Though the use of wood as a home heating fuel only comprises 4% of our national heating fuel budget (Annual Report of the Council on Environmental Quality (CEQ), 1983), the contribution of wood to the national energy budget has surpassed that of nuclear power and may increase fivefold by the end of the century (Smith, 1981).

The societies of industrialized countries have developed to the stage where the needs of daily survival are generally fulfilled and a growing emphasis is placed on increasing the longevity of human life. This has brought about an awareness of substances in air, water and food which might be harmful to human health. Hence the current concern over air pollution from wood fires is as much due to sociological, political and economic factors as it is due to the real increase in pollutant emissions from woodburning over the last two decades. Popular news magazines as well as local newspapers in the United States have featured articles on the concern about air pollution from residential woodburning. The number of people using wood for home heating reached a peak in the United States in 1950 and then decreased to a minimum in 1975; however, with the increasing costs of burning fossil fuels, the current number is approaching that of 1950. (CEQ 1983 Annual Report). An editorial cartoon in a local Oregon paper depicted the wood stove as a Trojan horse, with its evil hidden beneath its apparent good (Beyers, 1982).

I will examine, in this dissertation, the contribution of emissions from the burning wood for home heating fuel to urban air pollution in the United States. A gaseous tracer unique to woodburning in residential neighborhoods, CH_3Cl, is used to estimate fine particle concentrations of woodsmoke in the ambient air in several residential neighborhoods in and around Portland, Oregon. In Chapter 1, I will review the body of knowledge on which the concern for exposure to woodburning pollutants is based and discuss the previous models used to assess the contribution of wood combustion to urban pollution. In Chapter 2, a description is given of the

Chemical Mass Balance (CMB) and of the previous use of gaseous tracers in air pollution studies. The uncertainties of the CMB model are examined and the potential of reduced uncertainties with the inclusion of gaseous species in the model is discussed. Chapter 3 includes a description of the experimental techniques used in this dissertation. In Chapter 4, the results of source emission testing of wood stoves to determine the source emission factor for CH_3Cl is presented. Emission factors are also given for other gases, including CO, CH_4, benzene and toluene. This chapter includes an analysis of background concentrations of methyl chloride. The receptor model is applied to determine the contribution of woodburning to air pollution in several residential neighborhoods and compared with the results from the concurrent application of other models. In Chapter 5, the implications of this dissertation in assessing the contribution of wood combustion to urban air pollution is examined. The Summary includes a discussion of the potential extension of the Chemical Mass Balance model presented in this dissertation to broader applications.

The objectives of this work will be the development and testing of ambient and source characterization methods for CH_3Cl and other gases as applied to receptor models, the incorporation of gaseous as well as particulate phase species into the mass balance receptor model framework and verification that the CH_3Cl used in a tracer solution provides equivalent results.

CHAPTER 1

THE PROBLEM: Assessing the Contribution of Wood Combustion to Urban Air Pollution.

1.A. Health Concerns for Exposure to Pollutants from Woodburning.

While this dissertation does not attempt to demonstrate the existence of adverse health effects from exposure to pollution from wood combustion, the research work presented here does suggest novel methods of assessing those exposures through the application of gaseous tracers in receptor modeling. For many years there has been an awareness of the connection between adverse human health effects and air pollution. Polluted air has been associated with the common cold, acute and chronic bronchitis, pneumonia, emphysema, asthma and lung cancer (Williams et al., 1974). Historically, periods of recorded urban air pollution events can be associated with times of rapid population growth and economic deterioration. Two periods of well documented air pollution incidents in London around the year

1300, and again just after 1650 can be correlated with fuelwood shortages whereupon coal was substituted as the main fuel (Brimblecombe, 1982). It was not until 1952 when unusually poor conditions for meteorological dispersion combined with the increasing emission of air pollutants that the deaths of around 4000 people during an air pollution episode in London (Goldsmith and Friberg, 1977) demonstrated the truly devastating effects which human activities can have on one of the most important resources needed to ensure our survival: clean air. This event was indeed unique due to the length of the meteorological stagnation combined with the heavy coal use in the city. Other disastrous air pollution episodes have been documented when an unusual number of illnesses and deaths, mostly from diseases of the respiratory tract, occurred during periods of fog and temperature inversion near large sources of pollutant emissions. In November and December of 1962, many cities in the Northern Hemisphere reported increased pollution levels and excess numbers of illnesses or deaths (Goldsmith and Friberg, 1977). While the long term effects of air pollution caused by the slow accumulation of toxic materials are not as well documented, they may be even more harmful to human health.

Substantial progress has been made during the past two decades toward identifying the components of our atmosphere which might cause adverse health effects and their sources. This dissertation will examine the contribution of residential woodburning to urban atmospheres not only because of the potentially harmful health effects of the components of woodsmoke but also because it contributes, along with other sources, to the degradation of urban air quality.

Although humans have been exposed to the toxic compounds from wood combustion throughout their existence, it is only in the present day that we have become aware of the potential health problems associated with it. A study by Butcher (1978) developed particle emission factors for the burning of wood in home stoves and estimated worst case values of particulate pollution of up to 100 $\mu g/m^3$ from wood stoves in small communities of Maine. This is a substantial fraction of the 260 $\mu g/m^3$ which is the 24 hour national ambient air quality standard for total suspended particulate pollution. DeAngelis et al. (1979) characterized criteria pollutant emissions and polycyclic organic material (POM) from residential woodburning equipment finding large quantities of POMs including many carcinogenic compounds. In the Portland Aerosol Characterization Study (PACS), Watson (1979) and Cooper (1979a,b) provided evidence from ambient measurements, to which they applied the Chemical Mass Balance Model, that wood combustion was an important source of particulate pollution in an urban area. Cooper (1980) reviewed health concerns for emissions from residential woodburning and suggested that this source might become one of the more significant contributors to the nonattainment of an inhalable particulate standard.

Adverse Health Effects from Woodburning Emissions

The documentation on the direct health effects of exposure to large quantities of emissions from wood stoves has not kept up with the atmospheric studies. In identifying ambient air pollution related adverse health effects, a tremendous number of confounding variables come into play, such as exposure to cigarette smoke, occupational exposure, socioeconomic level, housing and gas cooking (Pengelly et al., 1984). A study in Missoula, Montana (Carlson, 1982) found high concentrations of total suspended particulate matter (TSP) and attributed these mostly to emissions from woodburning. The high concentrations of TSP were shown to cause measurable health effects in grade school children and people with chronic pulmonary disease. These health effects were expressed as a decrease in forced vital capacity (FVC) and forced expiratory volume (FEV) which are measures of the amount of air which can be exhaled after maximum inhalation and a measure of air flow rate. It is not known whether these effects are long term and cause permanant lung damage.

The existence of chronic health problems which include persistent or irreversible diseases of the respiratory system are of great concern in examining the health effects from woodsmoke. The mutagenic activity of woodsmoke particles has been demonstrated by Ames Salmonella /microsome bioassay tests (Lofroth, 1978; Lewtas, 1982; Rudling et al., 1982; Ramdahl et al., 1982; Alfheim et al., 1982). Quantitative estimation of human cancer risk from woodsmoke is extremely difficult, although cancer occurrence in persons chronically exposed to polycyclic aromatic hydrocarbons, persons with a history of cigarette smoking and those who habitually ingest smoked food is well documented (Busbee et al., 1980). The polycyclic organic matter (POM) found in woodsmoke and associated with carcinogenic compounds comprises 35% on an annual basis of total POMS emitted to the atmosphere in the U.S. (Peters , 1982).

The danger of acute health problems caused by high levels of gases and particulate matter found in woodsmoke is also a concern. Cilia toxic and mucus coagulating agents found in woodsmoke include aldehydes, phenols and cresols (DeAngelis et al., 1979). Aldehydes can irritate the skin, nose and throat, and formaldehyde has even been associated with dermatitis (Fisher et al., 1962). High concentrations of benzene, toluene and xylenes, which are also found in woodsmoke, can cause acute health effects including fatigue, muscle weakness and confusion in humans (Konietzko et al., 1980; Bennett et al., 1980). Benzene at concentrations of several hundred ppm is associated with local irritation, intoxication, central nervous system depression and death (Beall et al., 1981). Carbon monoxide is also a product of wood combustion and in homes with leaky stoves it may be possible that the CO concentrations could exceed 50 ppm, which over a long period may cause CO poisoning (Air Quality Criteria for CO, 1970). Exposure to a weekly average concentration of CO of 8 to 14 ppm may increase the risk of myocardial infarction (Ibid). Measurements of CO concentrations during cooking using biomass fuels in an unvented simulated village kitchen typical of those found in northwest India averaged 33 ppm and the peak concentrations were as high as 183 ppm (Smith et al., 1984). Abietic acid, which is linked to cases of asthma in the electronics industry (Sigman et al., 1976), may be found in woodsmoke in high enough concentrations to be a potential health hazard (Edgerton et al., 1985). Other effects from high concentrations of woodsmoke aerosols include reduced visibility and unpleasant odors sufficient to cause annoyance or the creation of discomfort in many individuals.

The greatest evidence to date linking woodsmoke to adverse health effects is from studies of respiratory illnesses in developing countries. In June of 1984 the World Health Organization released a report announcing that respiratory diseases have become the chief cause of death in developing countries, overtaking the traditional diarrheal diseases and malnutrition which have dominated health statistics for morbidity and mortality for many years. The diseases of most concern are acute respiratory infection (ARI) in children and chronic obstructive lung disease (COLD) in adults. The incidences of both of these diseases have shown a strong and statistically significant association with the number of hours spent near domestic fires (EWC Working Group on Health Correlates of Domestic Smoke Exposures, 1985).

With the realization that emissions from woodburning are significantly contributing to ambient air pollution, a need arises for an accurate quantification of the ambient contributions from this source. In Chapter 5, the advantages of using methyl chloride as a tracer of fine particle pollution in estimating acute exposures to pollutants from residential wood combustion will be presented. With accurate knowledge of the concentrations of woodsmoke to which people are exposed in residential neighborhoods, the potential adverse health effects may be better addressed.

1.B. Background: Previous Models and Estimates of Wood Combustion Contribution to Urban Ambient Air Particulate Concentrations

Since the dispersion model study by Butcher (1978) which suggested residential wood combustion could contribute up to 100 $\mu g/m^3$ to community air pollution, there has been much concern over exactly how much pollution may be attributed to this source. An early receptor model suggested for use in assessing the contribution from wood combustion was based on an enrichment factor approach. Potassium was assumed to be a tracer of woodsmoke, and a ratio of potassium to iron, K/Fe, in the aerosol over that in the soil greater than 1 was considered indicative of a woodburning contribution. Besides there being other sources for K, source testing of residential woodburning has shown that enrichment factors can vary by over an order of magnitude among the different types of wood combustion (Watson, 1979; Shah, 1981; Rau and Huntzicker, 1985a; Rau, 1985b). In the Portland Aerosol Characterization Study (PACS) of 1979, Watson applied the Chemical Mass Balance model, which will be described in the next chapter, and found that 30% of the fine particulate material in the wintertime in residential neighborhoods could be attributed to vegetative burning. Because of the high variability in the PACS source compositions of vegetative burning, two separate profiles were used, VBRN1 and VBRN2, to which average uncertainties of 20 and 40% respectively were attached. Watson suggested the estimated woodburning contributions be confirmed by identifying more unique chemical constituents in the source emissions.

Cooper et al. (1979b and 1981), demonstrated the use of the Carbon-14 (C-14) in woodsmoke particles to estimate the maximum impact of woodburning in Portland, Oregon. Atmospheric carbon particles can generally be divided into those of fossil or contemporary origin. The C-14 exchange with the biosphere is short, about 10 years, compared to its 5770 year half life. All material which has been dead for a short time relative to the half life will contain the equilibrium carbon-14 concentrations and fossil carbon will contain essentially no C-14. The C-14 component of the source composition includes corrections for: (1) the age of the burned material which will have experienced an activity decay, (2) for the increases in C-14 with nuclear weapons testing of the 1960s, and (3) for decreases resulting from the dilution of the average C-14 in CO_2 taken in by plant life due to the increasing proportion of atmospheric CO_2 from fossil fuel combustion. Even with corrections, the inclusion of C-14 in receptor models does not definitely quantify the residential wood combustion contribution to air pollution due to the presence of other C-14 sources such as municipal incinerators, hogged fuel boilers, gasohol combustion and particularly the formation of secondary particles from vegetative vapor emissions. Yet the carbon-14 measurements confirmed the findings of Watson that vegetative burning is a major source of fine particulate material in the Portland urban area.

By the 1980s many studies of urban air pollution found residential woodburning to be a major contributor to fine particle concentrations in the wintertime. Meyer, 1981, estimated that particulate concentrations from woodburning for an inversion capped valley calculated from a box model might reach 1000 $\mu g/m^3$. Dasch, 1982, employed ambient C-14 and K/Fe ratio measurements with relative particulate mass emissions to estimate the wintertime contribution of woodburning as 20-30% of the fine particle mass concentrations in Denver. Using ambient C-14 measurements, Ramdahl et al. (1984) estimated that wood carbon contributed 65% to the carbon of ambient fine particles in a community in Norway. Woodburning source compositions taken from ambient measurements on Christmas eve, when few other sources of fine particulate material were expected to contribute to the fine aerosol, were used in the CMB model to estimate the woodburning contribution in Medford, Oregon as 66% of the fine particle mass (DeCesar and Cooper, 1982). Peters (1982) examined relative emission factors for residential wood combustion and concluded that it was the largest contributor to polycyclic organic material (POM) in ambient air. Ramdahl et al. (1983) suggested using rentene, which is found in the PAH (polynuclear aromatic hydrocarbon) fraction of woodsmoke, as a distinguishing constituent of the woodburning component of the aerosol. This method has not yet been applied to the quantification of the wood combustion contribution to fine particle pollution.

In the last 5 years, dozens of studies characterized the emissions from woodstoves and attempted to quantify their contributions to air pollution in residential communities using both dispersion modeling and receptor modeling. The ability to estimate the contribution of wood combustion to air pollution using dispersion models is severely limited by the difficulty in accurately quantifying the emission factors which are highly variable in space and time. In addition, many of the dispersion models which have been commonly used and are easily available assume steady state conditions which often do not exist in the evenings when the woodburning emissions are the greatest. An Eulerian finite difference model was used by the Oregon Department of Environmental Quality and found to consistently underestimate the woodburning contribution, often by a factor of 2, of that found by the CMB model (Kowalczyk and Greene, 1982). An ideal dispersion model for estimating woodsmoke concentrations would be one which considers the spacial and temporal variations of area source emissions. The RAM model of Novak and Turner, 1976, was developed to handle hourly input meteorological and emission data for point and area sources and output hourly concentration values. The RAM model was considered for use in comparing the calculated and measured methyl chloride concentrations of this work, but was abandoned due to the model's inability to reproduce the concentration buildup typical of winter evenings. The shortcomings of the RAM model in reproducing temporal concentration variation, especially in the winter have recently been documented (Rao et al., 1985).

The estimation of the wood combustion contribution to air pollution by previous Chemical Mass Balance model studies using particulate phase species has been limited by the similarity in the woodsmoke source composition with that of other sources. This similarity results in a collinearity among independent variables included in the least squares solutions to the CMB equations. The solutions yield unrealistic source contribution estimates in these cases. If a species which is unique to one of the sources is included in the model, the collinearity is removed and realistic source contributions are obtained. It will be shown that the inclusion of methyl chloride as a characteristic species of woodburning in the CMB model substantially reduces the collinearity of the woodsmoke composition in situations where other common sources types are present.

Stephens and Burleson (1969) first suggested that methyl chloride might be used as a tracer of woodsmoke. However, the analytical techniques at the time were not sensitive enough to measure small increases in the atmospheric methyl chloride concentrations. It was later noted by Rasmussen et al. (1982) using more refined measurement techniques that elevated methyl chloride concentrations were found in rural China and these were attributed to smoldering combustion in home fires. A simple dispersion model was applied (Edgerton, 1981), using measured CH_3Cl/CO_2 emission ratios from wood combustion (Rasmussen et al., 1980b) and measured CO emission factors and estimated carbon conversion to CO and CO_2 in wood combustion (DeAngelis et al., 1979) to evaluate the feasibility of attributing ambient elevated concentrations of methyl chloride in the Portland, Oregon to residential woodburning. The dispersion study estimated the fine particle concentration from woodburning in $\mu g/m^3$ to be approximately 1/2 of the elevated CH_3Cl concentration in pptv and suggested that methyl chloride could be used as a surrogate real-time tracer for other ambient pollutants attributable to residential wood combustion. In 1981 a pilot study was conducted to measure CH_3Cl concentrations in suburban locations where it was evident that wood was being burned. The results of the study (Khalil et al., 1983a) agreed well with those of previous estimates of woodburning pollution by Cooper (1980, 1981). The methyl chloride approach for estimating the woodburning contribution to air pollution was formulated by Khalil et al. (1983) using measurements from the literature for CH_3Cl/CO_2 and CO_2/fine particle ratios to estimate the fine paricle/CH_3Cl emission ratio in wood combustion. It was suggested that given the current state of knowledge the CH_3Cl tracer method of estimating the woodburning contribution was only accurate to ± 50%.

In this work the methyl chloride tracer method of estimating fine particle pollution from woodburning has been refined. Direct measurements of the fine particle/CH_3Cl ratios in the source and two and one half years of measurements of the urban background concentrations of methyl chloride allow the estimates of fine particles from woodburning to be made with uncertainties less than ± 50% and as low as ±20% on evenings when there is considerable woodsmoke pollution. In addition, it is demonstrated that methyl chloride may be used as a characteristic species of woodsmoke in the standard CMB model. The CH_3Cl tracer approach is used to estimate pollution from woodburning in four residential neighborhoods in and around Portland, Oregon. The results are compared and found to be consistent with other receptor model approaches applied concurrently. The input requirements and the output information for the various models used to estimate the woodburning contribution are shown in Table 1.B.1.

In the next chapter, the formulation of the basic Chemical Mass Balance model will be described, the use of gaseous tracers in receptor modeling studies of air pollution will be reviewed and the uncertainties in the CMB receptor model estimates of the source contributions to air pollution will be discussed.

TABLE 1.B.1

Comparison of Requirements and Output for Methods Which Have Been Used For Assessing the Woodburning Contribution to Fine Particle Concentrations

METHOD	TYPE	INPUT REQUIRMENTS	OUTPUT
Emission Inventory	Source	Estimates of daily or annual emissions of all major sources	Relative woodburning emissions-no temporal or spacial resolution
Dispersion	Source	Estimates of hourly or daily emissions and corresponding meteorological data	Hourly values are valid only under steady state conditions for most models, not accurate for complex terrain. Predictive model.
Multicomponent Chemical Mass Balance	Receptor	Complete emission characterizations of chemical species for all sources and ambient measurements of chemical species	4-24 hour source contributions for sources which do not have collinearities with other source compositions
Carbon-14 Approach	Receptor	Carbon-14 ambient measurements, knowledge of other carbon-14 sources	24 hour maximum source contribution
Methyl Chloride Approach	Receptor	Methyl chloride/ aerosol emission ratios and background and ambient methyl chloride measurements	Woodburning contribution over short or long periods: 5 minutes to 24 hours

CHAPTER 2

APPROACH TO THE PROBLEM: Application of Chemical Mass Balance Model to Estimate Woodburning Contribution to Air Pollution

2.A. Formulation of the Chemical Mass Balance Receptor Model

The method of using material balances to relate particulate air quality to emissions was first developed and applied to the Los Angeles aerosol by Miller et al. (1972) and by Friedlander (1973). The basic chemical mass balance formulation assumes conservation of mass at the reference point of the receptor. The fundamental equation states that the mass of aerosol at the receptor, ρ , is the sum of contributions from j sources, m_j:

$$\rho = \sum_j m_j . \qquad (2.A.1)$$

To estimate source contributions, the assumption is made of the conservation of relative composition of the source emissions between the point of emission and the point of measurement at the receptor. The operational form of the Chemical Mass Balance (CMB) model will be described here and has been reviewed by several authors including Watson, 1979, Cooper and Watson, 1980, Core, 1981, and Henry et al., 1984. The concentration of the species i measured at the receptor, C_i, is:

$$C_i = \sum_{j=1}^{p} a_{ij} S_j \qquad (2.A.2)$$

where S_j is the contribution of the source type j to the total concentration of species i and a_{ij} is the mass fraction of species i emitted by source j. When n species and p source types are included in the material balance such that $p \leq n$, the S_j may be calculated by solving the overdetermined system of linear equations. The equation may be solved for the most probable value of S_j using the ordinary linear least squares method (Bevington, 1969) by minimizing the χ^2 , where:

$$\chi^2 = \frac{\sum_{i=1}^{n} C_i - \sum_{j=1}^{p} a_{ij} S_j}{\sigma_{c_i}^{2}} \qquad (2.A.3)$$

The σ_{c_i} represents the sampling and analytical uncertainty in the measurement of the concentration C_i measured at the receptor.

In matrix form the CMB equation is:

$$C = A\ S \qquad (2.A.4)$$

where C is a mxl vector of ambient concentrations, S is a nxl vector of source contributions and A is the mxn matrix of source compositions. The ordinary least squares solution to the problem is:

$$S \ = (A^TWA)^{-1}A^TWC \qquad (2.A.5)$$

(Draper and Smith, 1981),

where W is a diagonal matrix of weights $\sigma_{c_i}^{-2}$, the A^T is the transpose of A and the uncertainties of the S are the diagonal elements of the matrix $(A^TWA)^{-1}$. The solution is found by minimizing χ^2, as in equation 2.A.3. The ordinary least squares procedure assumes the uncertainties in the independent variables, in this case the source compositions A, to be negligible compared to the uncertainties in the dependent variables, the ambient concentrations C. Often this assumption is not met and the source compositions contain the largest uncertainties. The effective variance method of estimating the S_j as applied by Watson, 1979, and Dunker, 1979, and described by Watson et al., 1984, uses the solution of Britt and Luecke, 1973, to include the uncertainties in the source compositions. The uncertainties in the S are then the diagonal elements of the matrix $(A^TV_{eff}^{-1}A)$, where:

$$V_{eff}^{-1} = (\sigma_{c_i}^2 + \sum_{j=1}^{p} \sigma_{a_{ij}}^2 S_j^2)^{-1} \quad (2.A.6)$$

and $\sigma_{a_{ij}}$ is the uncertainty of a_{ij}. Because the effective variance method includes the uncertainties from both the source and receptor measurements and allows those measurements with greater precision to have more influence in the least squares solution, this method represents a more realistic estimate of the uncertainties in the S_j.

Until recently, the Chemical Mass Balance model has been applied separately to apportion the sources of elemental and of gaseous species. This dissertation combines gaseous and particulate phase species to apportion the sources of fine particulate material in the atmosphere. In the early applications of the model to elemental species, the model was called the Chemical Element Balance and the concentrations of the elements, C, were written in terms of the mass fraction of element i in the total particulate material (or fine particulate material) emitted from source j, a_{ij}, and the contribution to the total particulate concentration from source S_j. An example is given below:

C(element i) = a(mass fraction of element i in emissions of source j) x S(contribution of source j to total particulate mass). (2.A.7)

This is the most common application of the Chemical Mass Balance model.

In apportioning gaseous species, the concentrations C are the concentrations of the gaseous species written in terms of the mass fraction of gas i in the total gases times the contribution of the source j to the total gas concentration. An example is given for the source apportionment of hydrocarbon species:

C(hydrocarbon gas i) = a(mass fraction of
gas i in total hydrocarbon gaseous emission
in source j) x S(contribution of source j
to total hydrocarbon gases). (2.A.8)

The linear system of equations may be solved for the source contributions S to the total hydrocarbon gas concentrations just as in the case of the elemental model. Examples of the use of mass balance modeling using gaseous species is found in Mayrsohn and Crabtree, 1976 and 1977, and in Nelson et al., 1983.

A third approach combines the use of the gaseous and particulate phase species to estimate the contributions S_j of each source to the total particulate or gaseous concentrations. In this work it is demonstrated how gas phase species may be combined with particulate phase species to apportion ambient fine particulate matter. The ambient concentrations C_i are either of particulate or gaseous species and the corresponding a_{ij} for the elemental species are the same as those described in the chemical element balance approach. The a_{ij} for the gaseous species are the ratios of the gaseous emission factors to the fine particulate emission factors for the source of interest. An example of mass balance equation for a gas phase species is:

$$C(\text{gas } i) = a(\text{gas } i \text{ to particle ratio in emissions of source } j) \times S(\text{Contribution of source } j \text{ to particulate concentration}). \quad (2.A.9)$$

If the gaseous species has a known background concentration, the C represents the excess of the ambient gas concentration over the background concentration.

The approach incorporating both particulate and gas phase species represents an operational improvement over using only particulate phase species in the application of chemical mass balance modeling to apportion sources of air pollution because more of the potential chemical information is used to characterize each source. The inclusion of gaseous species may help separate source characterizations in cases where there exists an approximately linear relationship between two or more source compositions. This situation results in a collinearity in the source composition matrix and may cause the problem of solving the CMB equations to be "ill conditioned". This situation is discussed further in section 2.C of this chapter. In the next section a historical perspective is presented of the use of gaseous species in tracing the sources of air pollution.

2.B. The Historical Use of Gaseous Species in Tracing Sources of Air Pollution.

Receptor models including only particulate phase species are most commonly used to estimate air pollution source contributions. Volatile organic compounds have been used in a few receptor model studies. Stephens and Burleson, 1969, first suggested correlating the relative amounts of light hydrocarbons in the air with individual sources. They pointed out that the distribution of hydrocarbons in most urban ambient air samples generally matched that of auto exhaust with the exception of a few samples containing higher than normal amounts of the C2–C5 paraffins, which it was suggested could be attributed to commericial natural gas sources. They suggested acetylene could be used as a tracer for auto exhaust. They presented light hydrocarbon compositions for brush fire smoke, smog, an industrial area, a parking lot and a busy street corner. The existence of CH_3Cl in the brush fire smoke was mentioned and it was suggested that with more sensitive measurement techniques than were available at the time that CH_3Cl might make a good tracer for wood smoke. Stephens and Burleson also used acetylene, ethene and propene ratios to measure the extent of reaction for auto exhaust since these compounds have different rates of reactivity.

In addition to using gaseous compounds to estimate the contribution to urban pollution from industrial sources, some gaseous species may be used to identify general source areas of pollution and as tracers of long range transport. Lovelock in 1971 suggested using sulfur hexafluoride, SF_6, and trichlorofluoromethane, CCl_3F, as indicators of polluted air masses since these compounds are emitted only from industrial sources. He observed increases in the concentrations of both compounds in southwest Ireland in August of 1970 corresponding to easterly winds from continental Europe and coincidental with observed increases in atmospheric turbidity.

Simmonds et al., 1974, attempted to label the Los Angeles Basin with characteristic halogenated compounds using CCl_3F, CCl_4, $C_2H_3Cl_3$ and C_2Cl_4. They confirmed the typical diurnal meteorological pattern in the area by the observed diurnal variations in these compounds and suggested that $C_2H_3Cl_3$ and C_2Cl_4 have background sources which may contribute significantly to their concentrations because the vertical profile of these compounds remains constant above the inversion layer whereas the concentrations of the others continued to decrease with increasing altitude. Other studies demonstrated the use of the fluorocarbons in tracing air mass movements. Hester et al., 1974, showed how the fluorocarbon levels in L.A. followed patterns of high and low pollution episodes and tracked the movement of pollution from the L.A. basin downwind to Beaumont, California, with the onshore winds from the Pacific Ocean. The maximum fluorocarbon levels at an inland location corresponded to maximum ozone levels at another location the same distance downwind from L.A.

Volatile organic species were first used in a quantitative source apportionment by Mayrsohn and Crabtree, 1976, 1977, who performed multivariate regression analysis on hydrocarbons in L.A. to determine their sources. They applied the approach described in equation 2.A.8 to chemical mass balance modeling as discussed in the previous section. Prior knowledge of the six most likely contributors to volatile organic compounds in the L.A. Basin enabled Mayrsohn and Crabtree to estimate automotive, gas vapor, commercial gas and several other source contributions which would approximate the measured atmospheric profile. In a later study, Mayrsohn and Crabtree, 1977, included more sites and showed that the volatile organics from the coastal industrial sources were transported inland to desert communities over 150 km away. They did not address the potential change in the source ratios due to reactivity of the compounds. Nor did they consider the natural emissions from vegetation of longer lived species, such as acetylene (Rasmussen and Went, 1965; Rasmussen, 1972).

Singh (1977) compared the urban-nonurban relationships of some of the halocarbons and the differences in their concentrations between marine and nonmarine air masses suggesting possible natural sources for CH_3Cl, CH_3I, and CH_3Br. Lamb (1978) in a study of the release of tracers to characterize pollutant transport, suggested that the concentration of a pollutant from a source area could be related to the concentration of the tracer at the receptor if the emissions rates for both the pollutant and the tracer were known. Whitby and Altwicker (1978) discuss the use of various hydrocarbon/acetylene ratios to calculate auto contributions and photochemical losses of reactive species. They review other urban sources of acetylene.

Khalil, 1979, used the measured northern-southern hemispheric ratios of certain trace gases to estimate their southern hemispheric sources. Because the majority of industrial emissions take place in the northern hemisphere, a large southern/northern hemispheric ratio is a suggestion of natural emissions. The apportionment of the chlorocarbons and "greenhouse" gases, such as CO_2, CH_4, N_2O, to natural and anthropogenic sources is important to such concerns as: (1) climatic changes from their increased concentrations, including warming due to the greenhouse effect, and (2) stratospheric ozone depletion due to photochemical reactions. Rasmussen and Khalil, 1981, and Khalil and Rasmussen, 1982, found that global methane concentrations have been increasing with time. Methane levels are highly correlated with primary food production and energy use, suggesting the influence of anthropogenic sources on CH_4 increase. Gaseous tracers have also been used to identify the origins of arctic haze (Khalil, 1983b). The wintertime concentrations of trace gases in the arctic, such as the man-made halocarbons, are suggestive of long distance transport from the industrialized regions at the mid-latitudes of the northern hemisphere.

Nelson et al. (1983) calculated hydrocarbon source strengths in Sydney, Australia, for auto exhaust, petrol, petrol vapor, combined solvents and commercial gas sources. Industrial emissions were not well characterized due to their variability, so concentrations of the C2–C4 alkanes and olefins contributed by other sources were examined and unknown fractions were ascribed to process emissions.

Khalil et al, 1983a, applied a unique tracer characterization to apportion the contribution of woodburning to urban air pollution. When using gaseous species to apportion sources of particulate material, the assumption is made that simultaneously emitted gaseous and particulate species are equivalently transported between source and receptor. Expressed mathematically, f represents a transport coefficient and the concentration of the aerosol measured at the receptor, C_{aj}, from source j is a function of the source emission Q_{aj}:

$$C_{aj} = f\ Q_{aj} \tag{2.B.1}$$

The concentration of the gas i from source j measured at the receptor, C_{ij}, is:

$$C_{ij} = f\ Q_{ij}. \tag{2.B.2}$$

Combining equations 2.B.1 and 2.B.2, the concentration of the aerosol measured at the receptor from source j can be related to the concentration of the gas C_{ij}:

$$C_{aj} = (Q_{aj}/Q_{ij})\ C_{ij}. \tag{2.B.3}$$

If the emission ratio is denoted by :

$$\alpha_{ij} = Q_{aj}/Q_{ij} \tag{2.B.4}$$

then the basic equation for using a unique gaseous tracer resembles that of the tracer solution to the mass balance equations of Hidy et al. (1970) where the concentration of aerosol from source j is $S_{ij}(C_{ij}$ above):

$$S_{aj} = C_t/a_{t_j} = \alpha_{ij}\, C_{ij} \qquad (2.B.5)$$

and C_t represents the concentration of the tracer element t, and a_{t_j} corresponds to $(\alpha_{ij})^{-1}$ above.

A tracer gas i can be chosen which has a well characterized background concentration for use in the model. The concentration measured at the receptor, C_{ir} is then the background concentration, C_{io}, plus the concentration C_{ij}, contributed from source j. Equations 2.B.3, 2.B.4 and 2.B.5 then become:

$$S_{aj} = \alpha_{ij}(C_{ir} - C_{io}) \qquad (2.B.6)$$

Equation 2.B.6 represents the unique gaseous tracer approach to apportioning the contribution of source j to fine particulate pollution. Khalil et al., 1983a, suggest how this model may be extended to the use of multiple gaseous tracers of particulate pollution. In communities where the major interest lies in estimating the contribution of a particular source to air pollution, the unique tracer approach represents a simple and low cost method of single source apportionment if a tracer may be found for that source.

Often it may be more practical to consider using gaseous and elemental species together in mass balance modeling when the contributions of many sources are to be estimated. Many of the easily measured, relatively inert gaseous species have a multitude of sources which tend to add unneeded complexity to the model by demanding the inclusion of many source categories which cannot be easily characterized. For example, the source category of commercial solvent use would almost invariably have to be included in a gaseous mass balance model using hydrocarbon species. The variability of commercial solvent use from day to day, due to the many small commercial businesses which use solvents, creates large uncertainties in the CMB estimates of source contributions.

In the next chapter, the unique gaseous tracer approach will be applied to estimate the contribution of woodburning to urban air pollution in several residential neighborhoods in and around Portland, Oregon. The variability of the source emission factor and the background concentration of the trace gas is examined. The consistency of the results of the unique tracer approach with the results of other estimation techniques applied concurrently is examined. And finally, both particulate phase species and methyl chloride are used in the chemical mass balance model to estimate air pollution sources. In the next section the uncertainties in estimating source contributions with the chemical mass balance model will be examined. The advantage of including both particulate and gaseous phase species in the model will be demonstrated.

2.C. Comparison of Model Uncertainties in Estimating the Woodburning Contribution to Urban Air Pollution

The uncertainties in the source contributions calculated from the chemical mass balance effective variance solution, which takes into account the uncertainties in source compositions as well as the uncertainties in the ambient measurements, can be estimated when the absolute uncertainties of the receptor concentrations and source compositions are known. The uncertainties in the source emissions are rarely exact, but they are estimated by the standard deviations of values obtained in source sampling experiments. These experiments do not always include the systematic variability in the source emissions under varying conditions, and this variability may introduce uncertainties which are several orders of magnitude greater than the random error of measurements made under one condition. This is particularly true for elemental emissions from residential wood combustion. It is an issue that has never been fully addressed in previous attempts to characterize residential woodburning sources for inclusion in receptor models.

Watson (1979) and Watson et al. (1984) explored the effects of randomly perturbing input data to the CMB model. True simulated values for a_{ij} and S_j were combined to obtain true concentrations C . A random error, normally distributed and proportional to 10%, 20% and 30% of the uncertainty in the source and receptor measurements, was added to each value of a_{ij} and C_i. After 50 sets of data were created and used in a CMB calculation, the average S_j for burning from the 50 data sets, assuming 30% uncertainty in the variables, did not differ much from the true S_j; however the upper and lower ends of the range of calculated S_j from burning differed by a factor of 2 from the true value with the S_j value at one standard deviation differing by 39%. Although this study did not consider the effects of different uncertainty levels for different species, it did illustrate that there is a reasonable chance that the model may over- or under- estimate the true S_j by a factor of ± 40% when uncertainties exceed 20%. Uncertainties in the woodburning source composition of particulate species are over 20% for all of the characteristic species except organic carbon and methyl chloride, and even greater than 100% for species such as potassium and chlorine.

The average emission ratios of potassium/(fine particle mass) vary over two orders of magnitude. The percent of potassium (K) in woodsmoke aerosol from burning softwood and hardwood under cool burning conditions with a closed damper is 0.06% and 0.11%

respectively while the percent under hot burning conditions with an open damper is 11.6% and 5.8% (Rau and Huntzicker, 1985a and Rau 1985b). If the input data uncertainties were to reflect this variability, the weighting of K, which has been considered an important element for assessing the woodburning source, would be so low that K would become totally ineffective as a species for estimating residential woodburning contributions to urban aerosol. The coefficient of variation of the fraction of several species found in the woodstove source emissions in previous receptor models to apportion the woodburning source is shown in Table 2.A.1. This coefficient is defined as the square root of the variance divided by the mean value for the fractional composition as determined from the source sampling experiments of Chapter 4 and equations 4.A.1 and 4.A.2. In Chapter 4, section A, the variation of CH_3Cl/Mass from woodburning will be examined and compared to that of other species. It appears that of all the species which are important to the woodburning source characterization, CH_3Cl and organic carbon have the least variablity in source emissions. In a study by Cooper et al. (1984), uncertainties in the chemical mass balance estimates of the 24 hour maximum impact of woodburning on fine particle concentration range from 23 to 90%. However, the consistency of the chemical mass balance results with those of the carbon-14 approach lend greater confidence in the apportionment estimates.

In the single gaseous tracer approach to apportioning the woodburning source, small uncertainties may be propagated to include errors in the ambient measurements and in the gas/particle source emission ratio (Khalil et al., 1983). The uncertainties in the source ratio, α, and in the measured concentrations of the tracer gas at the receptor, C_{ir}, and in the background, C_{io}, may be propagated to give the estimated uncertainty in the source contribution, S_j, to the aerosol from the i^{th} source in equation 2.B.6.:

$$
\begin{aligned}
\sigma_{S_{aj}}{}^2/S_{aj}{}^2 &= \sigma_\alpha{}^2/\alpha^2 + \sigma^2_{(C_{ir}-C_{io})}/(C_{ir} - C_{io})^2 \\
&= \sigma_\alpha{}^2/\alpha^2 + \sigma_{C_{io}}{}^2/C_{io}{}^2(C_{ir}/C_{io} - 1)^{-2} \\
&+ \sigma_{C_{ir}}{}^2/C_{ir}{}^2\ (1 - C_{io}/C_{ir})^{-2} \qquad (2.C.1)
\end{aligned}
$$

where the σ's represent the experimentally determined estimated errors of the mean values. It can be seen from the uncertainty propagation that it is desirable to use in the model a gas with a low background concentration or a high C_{ir}/C_{io} ratio. In applying equation 2.B.6 to estimate the contribution of residential woodburning to urban aerosol, the values for the relative uncertainties will be shown in Chapter 4, sections A and B, to be:

$$\sigma_\alpha / \alpha = 0.10$$

$$\sigma_{C_{io}} / C_{io} = 0.02$$

$$\sigma_{C_{ir}} / C_{ir} = 0.02 \qquad (2.C.2)$$

where C_{io} is the background concentration of the tracer gas CH_3Cl at a rural site with little relative influence on the aerosol concentration from woodburning, and C_{ir} is the concentration measured at the receptor site. The α represents the ratio of fine particle to CH_3Cl mass in the emissions from woodburning stoves and this value and its uncertainties are discussed in detail in Chapter 4. The percent uncertainty in S_j for typical values of C_{ir}/C_{io} is generally between 20 and 40%. The uncertainty is reduced as the contributions from woodsmoke to the ambient particulate levels increase. This is demonstrated by Figure 2.C.1. and Table 2.C.2. It can be seen that for contributions less than 20 $\mu g/m^3$, the uncertainty becomes equal to or greater than the estimated contribution itself. Therefore given the experimentally determined values for the estimated errors, an elevation of 20 pptv CH_3Cl can be considered a lower limit for the application of CH_3Cl as a unique tracer. At large concentrations of woodsmoke aerosol, $S_j \geq 120$ $\mu g/m^3$, an equal contribution to the uncertainty in S_j comes from the uncertainty in the emission ratio α and that in the background CH_3Cl concentration. At smaller concentrations the uncertainty in the background concentration of the tracer gas contributes the most to the uncertainty in S_j . It is assumed that no uncertainty arises from possible other sources of the trace gas in this calculation. The model estimates with high confidence the contributions of woodsmoke in the air when they are high enough to be a health concern (in Chapter 4 this will be discussed in detail). These contributions are estimated with a much lower degree of confidence when the concentrations are very low and probably not of much importance as an air pollution problem.

Basic conditions for use of gaseous tracers in receptor models which estimate the contributions to particulate pollution are (1) the gases must have known background concentrations with elevations of concentration above background detectable at a significant level; (2) the ratio of the gas to the fine aerosol concentration at the source must remain constant during transport to the receptor; (3) the tracers should be well characterized in the sources of interest; and (4) there must be a high analytical sensitivity of measurement of the gaseous species.

The uncertainty in the source contribution estimates from the CH_3Cl tracer technique becomes large at low contributions due to the uncertainty in the background tracer concentration. One of the inadequacies of previous applications of the multicomponent chemical mass balance model is the incomplete specification of the uncertainties in source contributions due to the presence of background aerosol. Often rural and urban receptors are both treated as urban sites and CMBs are performed at both sites. Comparison can then be made between source contributions at the urban site and those at the upwind background site. It may be impossible to estimate the true uncertainties in the background aerosol at the urban site unless perfectly steady wind conditions are present during the sample collection period. Often changing wind directions can contaminate the background sample with urban aerosol which is later blown back over the urban site. The unique tracer model can easily include the uncertainty due to error in the estimated background concentration. This is discussed in detail in Chapter 4, section B. A calculation of the error in model source apportionment due to background error has never been fully addressed in multicomponent models. The carbon-14 unique tracer approach for estimating residential woodburning contribution must also take into account the background concentration of modern carbon from other sources such as the formation of secondary particles from vegetative vapor emissions and from emissions brought into the area by long range transport, from municipal incinerators, hogged fuel boilers and the increasing use of gasohol. While source estimates of woodburning contributions to ambient fine particle pollution have been made from radiocarbon measurements and shown to be consistent with expected residential woodburning impacts (Cooper et al., 1979b), the uncertainties due to possible other sources of modern carbon need to be evaluated.

Recently, simulated data sets were prepared to assess the state of the art of source apportionment procedures (Currie et al., 1984). One of the conclusions was that none of the reported results from participating laboratories included a completely adequate evaluation of model uncertainties and that generally the estimated uncertainties were too small. The best solutions gave results within about 30% of the true source contributions while on the average the true contributions were estimated within a factor of 2. It appears that in the absence of collinearities, the unique gaseous tracer method of source apportionment for residential woodburning is as accurate as the chemical mass balance methods and is more accurate than CMB model estimates where the woodburning source composition has a collinear relationship with another contributing source composition.

Henry, 1982, used the singular value decomposition technique to determine the number of sources that can be estimated to a given level of accuracy in a CMB calculation with a given source matrix and uncertainties in the ambient concentration matrix. This technique was later extended to include the error in the source composition matrix (DeCesar et al., 1985). DeCesar et al. demonstrate how the inclusion of a unique species in the source matrix can dramatically reduce uncertainties in source apportionment when collinearities are present. Previous CMB studies done in Medford, Or. (DeCesar et al., 1982) were unable to separate veneer dryer emissions from residential woodburning sources. The presence of a raw wood dust source also added to the uncertainties in the woodburning source estimates. By including CH_3Cl in the woodburning source composition, the uncertainties in the CMB calculation were greatly reduced as shown in Figure 2.C.2.

The singular value decomposition of the weighted source composition matrix A is:

$$A = UDV^T \qquad (2.C.3)$$

where U is a matrix whose columns are the eigenvectors of $A A^T$, V is a matrix whose columns are the eigenvectors of $A^T A$, and D is a square diagonal matrix whose diagonal elements, μ, are called the singular values of A . Near linear dependence among the columns of A , or among the source compositions, can be identified by the presence of small singular values. The inverse of the singular value corresponding to a source type is the upper limit for the precision with which that source may be estimated (Silvey, 1969).

The condition number $\kappa(A)$ provides a measure of the sensitivity of the least squares solution of the CMB equation to perturbations in the variables. If the measured C (or A) is perturbed by some small amount δC (or δA), it is of interest to determine how this will change S:

$$C = A\ S$$

$$C + \delta C = A(S + \delta S)$$

$$\delta S = A^{-1}\ \delta C. \qquad (2.C.4)$$

Just as the Euclidean norm of a vector is the magnitude of that vector, the spectral norm of a matrix is a scaler quantity that in some sense can be associated with the magnitude of the matrix. The spectral norm of A is the maximum singular value:

$$\| A \| = \mu\ \max \qquad (2.C.5)$$

and the spectral norm of A^{-1} is:

$$\| A^{-1} \| = \mu\ \min. \qquad (2.C.6)$$

Because of the properties associated with spectral norms (Belsley et al., 1980), equation 2.C.4 may be written as:

$$\| \delta S \| \leq \| A^{-1} \| \cdot \| \delta C \| \qquad (2.C.7)$$

and

$$\| C \| \leq \| A \| \cdot \| S \|. \qquad (2.C.8)$$

Therefore:

$$\| \delta S \| / \| S \| \leq \| A \| \cdot \| A^{-1} \| \quad \| \delta C \| / \| C \| \qquad (2.C.9)$$

and

$$K(A) \equiv \| A \| \cdot \| A^{-1} \| \qquad (2.C.10)$$

is the condition number. A similar derivation may be carried out for perturbations in A. The concept of the condition number can be extended to rectangular matrices (Belsley et al., 1980). Large K(A) implies that small perturbations in A and in C will produce large relative perturbations in S and therefore the least squares problem is "ill conditioned." The solution becomes unstable and unrealistic source contribution estimates can occur. For purposes of comparison the i^{th} condition index associated with each singular value is defined as:

$$\eta_k = \mu \max / \mu_k \qquad (2.C.11)$$

and it can be seen that the maximum condition index is also the condition number of the matrix. Belsley et al., 1980, suggest that a condition index higher than 30 might indicate a collinearity which degrades, or suggests low confidence in, the solution to the least squares problem.

Variance decomposition may be used in conjunction with singular value decomposition to help identify which source compositions contain collinearities. The variance decomposition matrix is called the Π matrix and is calculated from the V matrix used in the singular value decomposition. The elements of the Π matrix are calculated as follows (Belsley et al., 1980):

$$\pi_{jk} \equiv \phi_{kj}/\phi_k \quad , \quad k,j = 1,\ldots,p;$$

$$\phi_{kj} = v_{kj}{}^2/\mu_j{}^2 \quad , \text{ and}$$
$$\phi_j = \sum_{k,j=1}^{p} \phi_{kj} . \quad . \qquad (2.C.12)$$

Each column of the Π matrix is associated with a source type and the elements of the column add to 1. Within the column the variances are apportioned among the singular values or among the condition indices.

For a matrix with orthogonal columns all of the variance will be associated with an individual singular value and no two sources will have their variance associated with the same singular value. For sources which contain collinearities, the majority of the variance of those sources may be associated with the same singular value. Therefore, by looking at the Π matrix, one can identify which sources contain collinearities.

A hypothetical data set was constructed to demonstrate the effectiveness of these techniques in identifying collinearities (DeCesar et al., 1985b). Sources and their impacts included in this data set were those that might typify a winter sample in Portland. The hypothetical impacts were residential wood combustion, 40%, urban dust, 7%, residual oil, 1%, kraft recovery boiler, 5%, steel electric arc furnace, 2.5%, transportation, 10%, incineration, 8%, and coal fired power plant, 3%. The source profiles used were from the NEA source library (NEA, 1984). If only elemental species are used, the Π matrix is as shown in Table 2.C.3. Note the high condition number of the matrix, $K(A) = 502$, which is also the condition index with which both kraft and wood combustion have the majority of their variance associated. Including methyl chloride in the source characterization, the Π matrix can be recalculated and is shown in Table 2.C.4. The condition number is now less than 30 and the variance of the kraft is now associated with this index, while the variance of wood combustion is associated with a different index of 5.8. The two sources are no longer collinear. The relative uncertainty in the woodburning contribution also drops to about 30% where previously it was many times greater than the contribution itself. This example illustrates the use of unique species, whether gaseous or particulate, in breaking collinearities between source compositions.

With the use of singular value decomposition and variance decomposition as described by DeCesar et al., 1985b, the source compositions in a community may be evaluated for collinearity problems in estimating source contributions. The use of these tools in the design phase of a chemical mass balance model study will enable optimum allocation of resources in determining which species should be measured in a receptor modeling study.

It is concluded that source apportionment studies using methyl chloride may estimate the contribution of residential woodburning to ambient urban aerosol to generally within 20-40%. With improvements in our understanding of the health effects of exposure to the various species in woodsmoke, it may be desirable to develop techniques to identify the woodburning contribution with greater accuracy. However it may be even more important to characterize exposures to woodsmoke in indoor environments where wood is being burned. With current source apportionment techniques the woodsmoke component of the aerosol may be estimated with enough confidence for a community to decide if it is an important local source of air pollution.

TABLE 2.C.1

Coefficient of Variation in Source Emissions of Chemical Species Characteristic of Woodstoves from the Stratified Sampling Scheme. The coefficient of variation in the stratified sampling scheme is defined as the square root of the variance in Equation 4.A.2 divided by the mean of Equation 4.A.1. The number in parentheses is the sample size. Preliminary data only were available for particulate species.

Chemical Species	Coefficient of Variation % of fine aerosol mass
Organic Carbon	11 (11)
Elemental Carbon	71 (11)
Total Carbon	14 (11)
Potassium	299 (13)
Chlorine	296 (13)
Methyl Chloride	10 (36)
Carbon Monoxide	36 (36)
Methane	49 (36)

TABLE 2.C.2

Contribution to Relative Uncertainty of Woodburning Source Apportionment of Fine Particle Pollution from Uncertainties in the Source Ratio, α, and Measured Concentrations C_{ir} and C_{io} in Equation 2.C.1 of Methyl Chloride

S_j		σ_{S_j}		% Relative Contribution from Terms in Equation 2.C.1	
μg/m^3			C_{ir}/C_{io}	Term 1 (Source Ratio α)	Term 2 (C_{ir}/C_{io})
15	±	12	1.04	1	99
20	±	13	1.06	3	97
40	±	13	1.11	9	91
60	±	14	1.17	17	83
80	±	16	1.22	26	74
100	±	17	1.28	35	65
120	±	18	1.33	42	58

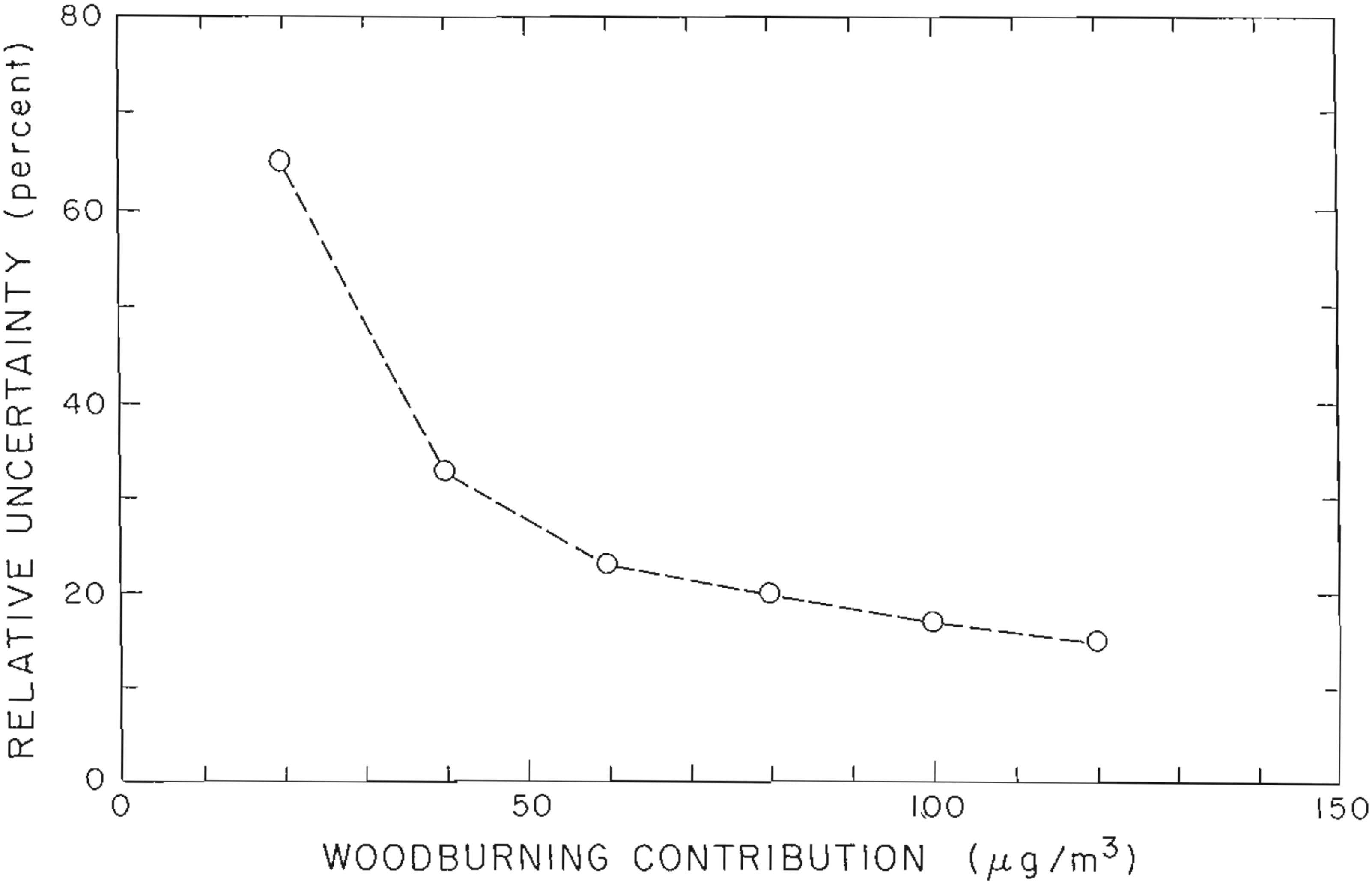


FIGURE 2.C.1: The % Relative Uncertainty in the Estimate of the Concentration of Particles from Woodburning Using the CH_3Cl Tracer, as a Function of the Woodburning Contribution

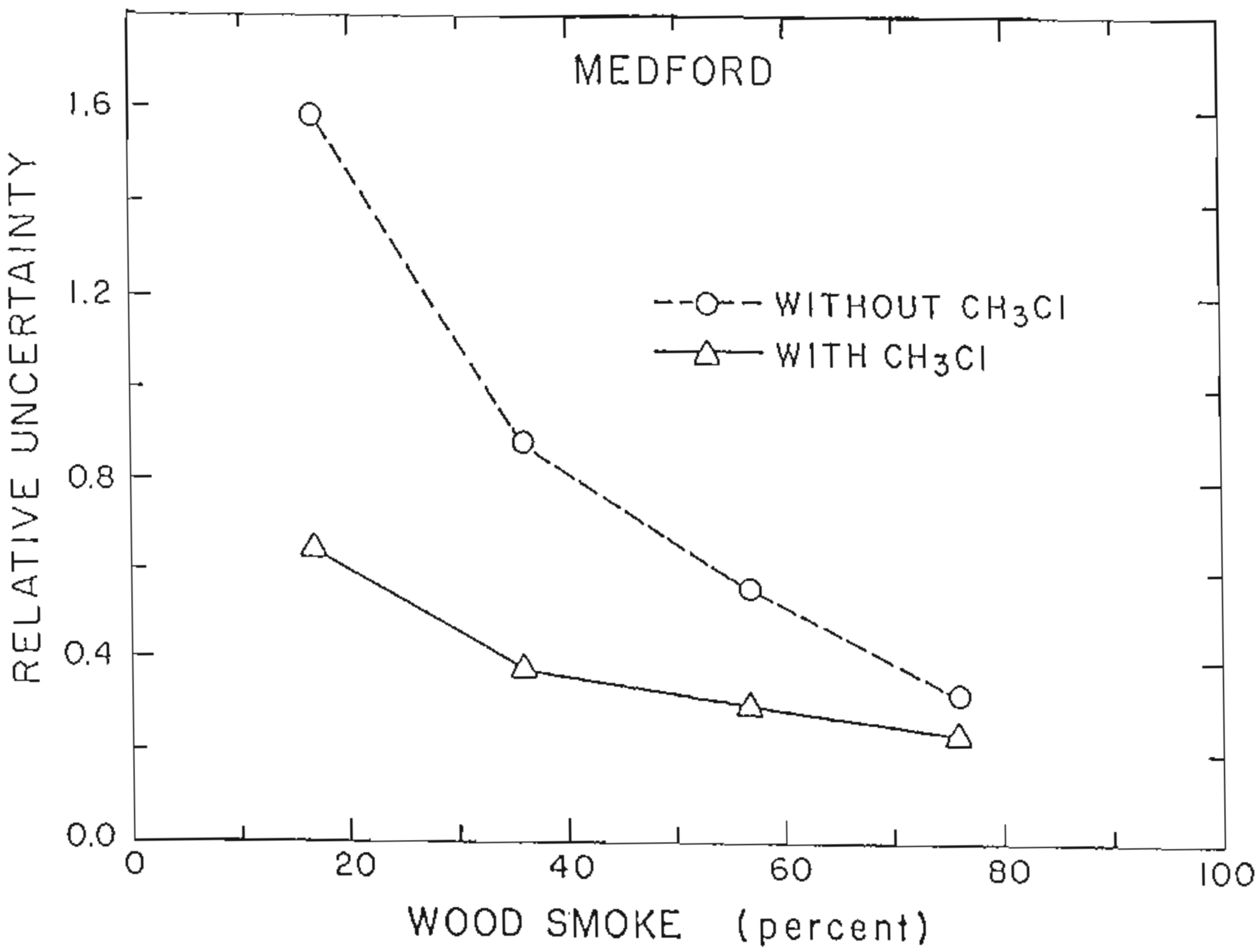


FIGURE 2.C.2: Comparison of the Upper Limit of Precision Attainable for Estimates of Woodburning Contribution to Fine Particle Concentrations With and Without CH_3Cl in the Model for Medford, Oregon, Calculated from the Singular Value Decomposition of the Source Composition Matrix

Test - Level 1

Table 2.C.3

Variance Decomposition Matrix for Hypothetical Data Set
Using Only Elemental Species

		Proportions of Variance							
Sing. Value	Cond. Index	Urban Dust	Residual Oil	Kraft Recovery Boiler	Steel Electric Arc	Transportation	Coal-Powered Plants	Woodsmoke	Municipal Incinerators
0.79	1.0	0.000	0.731	0.000	0.068	0.000	0.002	0.000	0.018
0.68	1.2	0.000	0.155	0.000	0.119	0.001	0.003	0.000	0.483
0.60	1.3	0.001	0.084	0.000	0.539	0.000	0.018	0.000	0.253
0.43	1.8	0.003	0.000	0.000	0.129	0.001	0.711	0.000	0.000
0.29	2.7	0.001	0.000	0.000	0.006	0.970	0.008	0.000	0.021
0.14	5.7	0.973	0.000	0.000	0.129	0.023	0.256	0.000	0.000
0.04	21.1	0.023	0.000	0.044	0.001	0.001	0.000	0.000	0.179
0.00	501.9	0.000	0.029	0.956	0.010	0.004	0.001	1.000	0.044

Table 2.C.4

Variance Decomposition Matrix for Hypothetical Data Set Using Elemental Species and Methyl Chloride

		Proportions of Variance							
Sing. Value	Cond. Index	Urban Dust	Residual Oil	Kraft Recovery Boiler	Steel Electric Arc	Transportation	Coal-Powered	Woodsmoke	Municipal Incinerators
0.79	1.0	0.000	0.752	0.000	0.069	0.000	0.002	0.000	0.019
0.68	1.2	0.000	0.160	0.000	0.120	0.001	0.003	0.000	0.508
0.60	1.3	0.001	0.087	0.000	0.546	0.000	0.019	0.000	0.266
0.43	1.8	0.003	0.000	0.000	0.131	0.001	0.713	0.000	0.000
0.31	2.6	0.001	0.000	0.000	0.005	0.884	0.010	0.003	0.021
0.14	5.6	0.946	0.000	0.000	0.123	0.050	0.246	0.019	0.000
0.14	5.8	0.025	0.000	0.000	0.005	0.063	0.008	0.972	0.000
0.04	21.5	0.024	0.000	1.000	0.001	0.001	0.000	0.006	0.185

CHAPTER 3

EXPERIMENTAL TECHNIQUES: Methodology For Gas and Aerosol Measurements

3.A. Sampling and Analysis of Gaseous Species

Ambient air samples were collected in 0.8 L stainless steel flasks which have been electropolished using the SUMMA® process, which produces an inert passive surface allowing for storage of the samples without affecting the concentrations of many gases. The air was pumped into the sample container with a metal bellows pump to ensure minimum contamination of the sample and the sample lines and flask were flushed with ambient air for 2-3 minutes. The air was collected over a few minutes until pressures of 20-35 psig were reached. The sample containers were flushed with purified air for one hour between use. The sample collection procedures have been described by Rasmussen and Khalil, 1980a. A description of the integrated sampling methodology is found in Appendix B.

The gas concentrations reported were measured using gas chromatagrophy (GC) techniques. Methyl chloride measurements were made using a Perkin-Elmer 3920 GC with a ^{63}Ni source electron capture detector (ECD). The measurement techniques have been previously described by Rasmussen et al., 1980b and Rasmussen and Khalil, 1980a. The output signal of the ECD was integrated using a HP 3390 system and the peak heights were verified on a chart recorder. The comparison of peak heights has been shown to provide a more accurate and reproducible measurement of the response than that of peak areas (Rasmussen and Khalil, 1980a). The precision of analysis for CH_3Cl as determined from the standard error of the mean of the peak heights from 4 to 5 repeated injections of the standard over each day of laboratory analysis is less than 3%.

Concentrations of CO, CO_2, and CH_4 were measured by a Carle 211-MS gas chromatograph with a flame ionization detector (FID) and molecular sieve column. The chromatographic peaks were integrated using a HP 3390. The precision of measurement for CO and CH_4 determined manually was 2% and 1% respectively (Rasmussen and Khalil, 1980a). Hydrocarbon gases such as benzene, toluene, isoprene, α-pinene, ethylbenzene, m+p-xylene and o-xylene were measured using a

Perkin-Elmer 3920 gas chromatograph with a flame ionization detector and a 30 M SE-30 fused silica column. A cryogenic concentration step was used and the GC/FID was temperature programmed to operate between -70°C and 100°C at a rate of 4°C/min. The peaks were integrated with a HP 3390. An internal neohexane standard was used and the absolute concentrations were based on NBS standards. The precision of measurement for benzene and toluene was ±10%. The source samples were analyzed in the same manner as the ambient samples but were diluted by a ratio of 100/1 with zero air from an Aadco clean air generator.

The working standards are contained in 35 L tanks which, because of their large volumes, have proven to be ideal for long term storage. These tanks have been tested in interlaboratory calibrations (Rasmussen and Khalil, 1981b). Once calibrated against the primary standard the stability of the secondary standard can be checked by establishing a pool of 4 tanks which are analyzed against the secondary standard at monthly intervals. The calibration of 4 tanks for CH_3Cl against the secondary standard ID# 0-165, which has a CH_3Cl concentration of 600 pptv, is shown in Table 3.A.1 and Figure 3.A.1. for the period over which the CH_3Cl measurements in this dissertation were made. The tank ID# 0-202 was used as the working standard for these measurements. The largest deviation of any of the tanks over the period is 6% and the largest deviation of 0-202 is 3%.

Because it is unlikely that all the tanks would drift together it can be assumed that the CH_3Cl concentration is stable in the standard containers and is neither produced nor detroyed. In the next section the stability of the sample containers for CH_3Cl will be examined.

TABLE 3.A.1

Methyl Chloride Concentrations in Laboratory Standards Calibrated Versus 0-165

Calibration Date	Standard Bottle			
	0-202	0-206	0-244	0-215
4/82	599 ± 9*	-	-	-
7/82	601 ± 4	-	-	-
10/82	594 ± 3			
2/83	589 ± 4	598 ± 4	644 ± 4	674 ± 8
7/83	-	-	637 ± 4	671 ± 3
8/83	582 ± 4	591 ± 3	-	-
5/84	606 ± 2	591 ± 4	604 ± 4	653 ± 4

*± value indicates the standard error of the mean
Value for 4/82 determined from GC-MS measurement

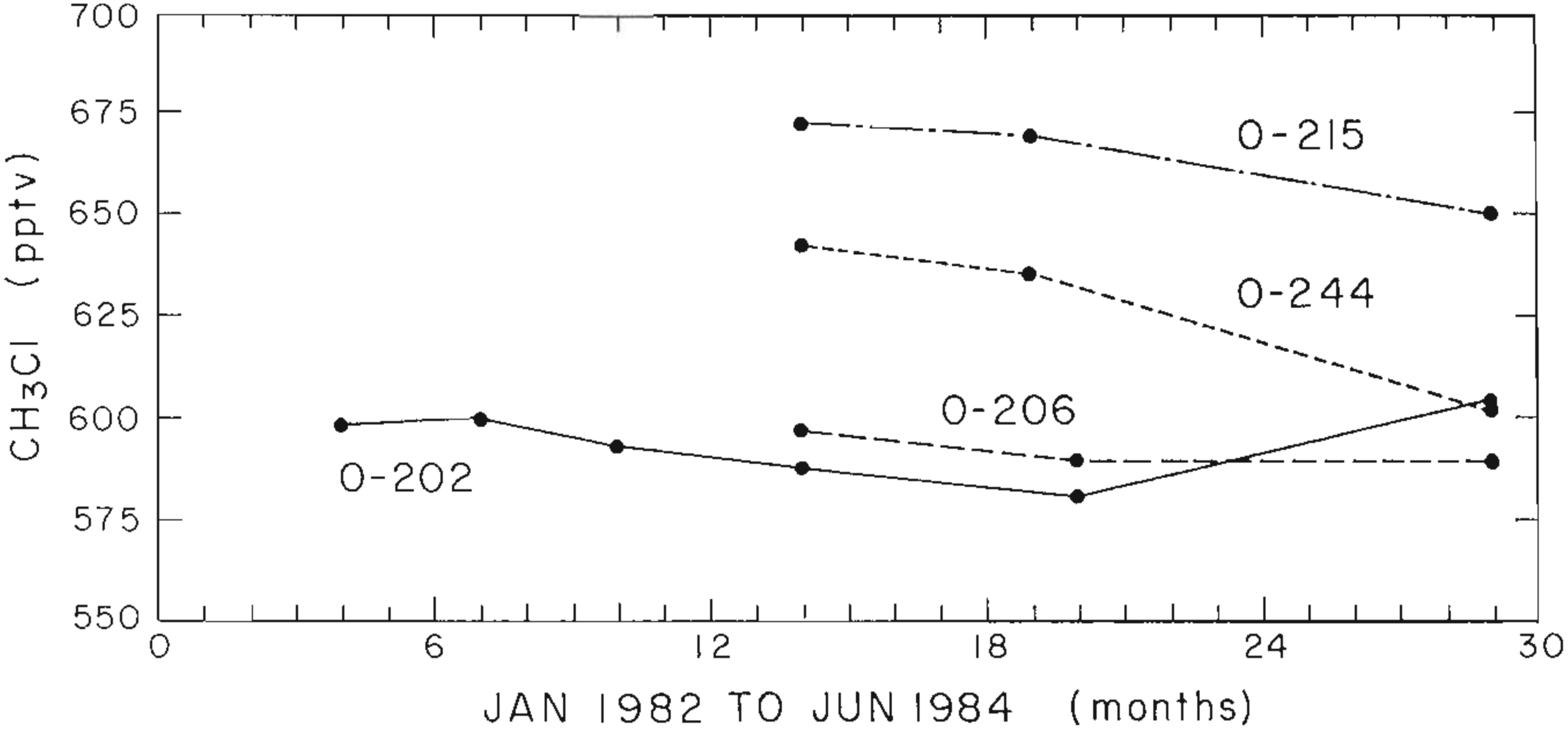


FIGURE 3.A.1: Long Term Stability of CH_3Cl Standards in 35 L Tanks

3.B. Stability of Methyl Chloride in Sample Containers

The concentrations of CH_3Cl in background global samples have been shown to remain constant in the 0.8 L sample containers over periods of long term storage (Rasmussen and Khalil, 1980a). Because of the presence of many other compounds at relatively high concentrations in urban air, a stability study of the flasks was conducted by repeated analyses of air samples over a period of several weeks. The flasks were equipped with steel or brass Nupro 4H4 metal bellows valves. The short term stablity (4 to 12 days) of the concentration of CH_3Cl in the containers is shown in Figure 3.B.1 and 3.B.2. as a histogram of the % deviation of the concentration after a few days from the original concentration. Flasks with deviations greater than $\pm$10% were labeled unstable and not used in this study. Forty one of the one hundred and nine flasks tested for stability were not used because of the lack of stabiliy of methyl chloride in them. The flasks equipped with steel valves which were used, n=46, showed a mean deviation of +1.4 ± 0.8% (± denotes standard error of the mean). The mean deviation of the flasks with the brass valves which were used in the study, n=22, was + 3.4 ± 1.1%. The flasks with brass values were not as stable with respect to CH_3Cl concentrations as those with steel valves (t test, α = 0.01).

Forty one of the stable flasks were analyzed for long term stability (1-3 month) and the results are shown in a histogram in Figure 3.B.3. The modal mean deviation (those with deviations less than ± 10%) of the concentrations of CH_3Cl over the longer period from the original concentration was +1.4 ± 0.8% and the concentrations in 11 of the flasks had increased more than +10%, while the concentration in 1 of the flasks decreased more than 15%. Throughout the period of the study, suspect fasks and others chosen randomly were reanalyzed for stability and in four cases the flasks were found no longer suitable for use in the collection of urban gas samples for CH_3Cl analysis. In 88% of the unstable flasks the concentration of CH_3Cl was found to increase with time. The mechanism for the production of CH_3Cl in the sample containers is not understood. Concentrations of CH_3Cl in urban samples which were collected in containers found to be unstable were consistently high, occasionally by as much as a factor of 3 compared to concentrations in stable containers. Samples were analyzed in the laboratory within 2 or 3 days of collection to minimize stability problems. However the fact that 39% of the sample collection containers which had been treated and accepted for use in the collection of clean air samples were found unsuitable for use in the urban air study illustrates the necessity for stability testing all containers to be used in a study of urban methyl chloride concentrations.

The 35 L containers used in the integrated sampling were also analyzed for stability of CH_3Cl concentrations over time. The short term stability results are shown in a histogram in Figure 3.B.4. The modal mean deviation (deviations $< \pm 10\%$) is $+2.9 \pm 1.3\%$ over 4 to 10 days and 7 of the 10 tanks tested deviated less than 10% from the original concentration. The three tanks in which the concentration deviated more than 10% from the original concentration were not used in the study.

The results of the stability analysis indicate that some individual containers may not be suitable for urban sample collection of ambient air to be analyzed for CH_3Cl. In more than one third of the containers tested, concentrations of methyl chloride increased over a period of one week by a factor much greater than the typical excess methyl chloride measured on an evening when wood is being burned. Therefore all containers to be used in a study of CH_3Cl in urban air should be tested before use. This is a very critical part of a study where small excesses in methyl chloride concentration are to be resolved. In the next section the sampling and analysis of the aerosol is discussed.

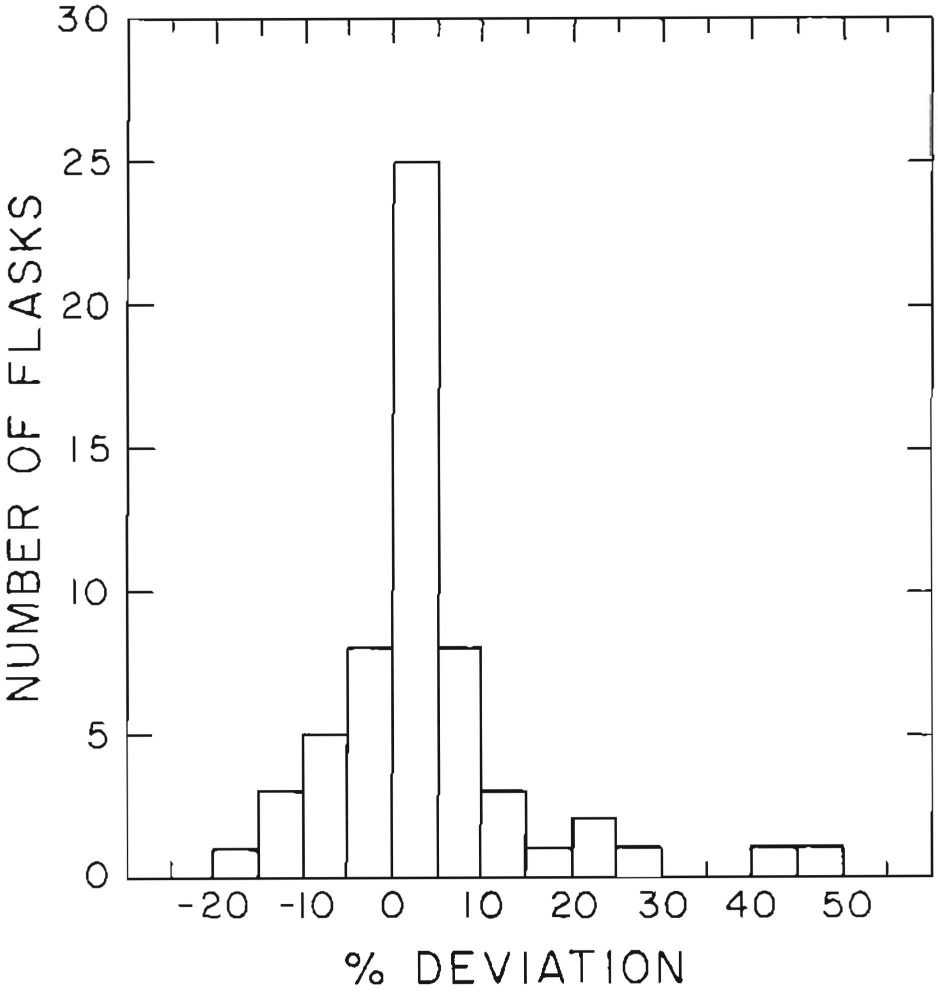


FIGURE 3.B.1: Short Term Stability of CH_3Cl in Small Sampling Flasks with Steel Valves. The number of samples deviating from the original concentration after short term storage of 4-7 days is shown. Three flasks showed concentration deviations greater than 100% and are not shown in the histogram.

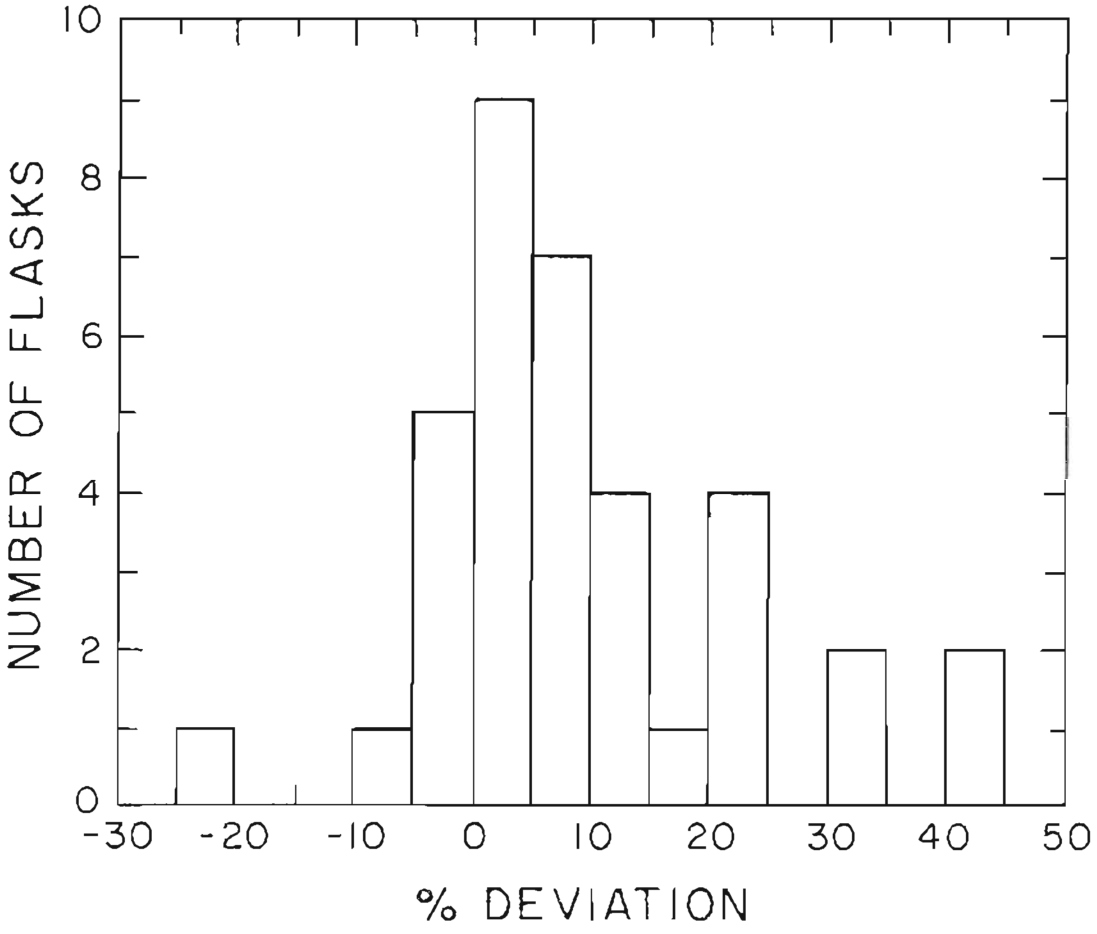


FIGURE 3.B.2: Short Term Stability of CH_3Cl in Small Sampling Flasks with Brass Valves. The concentration of 11 of the flasks deviated more than 100% after short term storage and are not shown in this histogram.

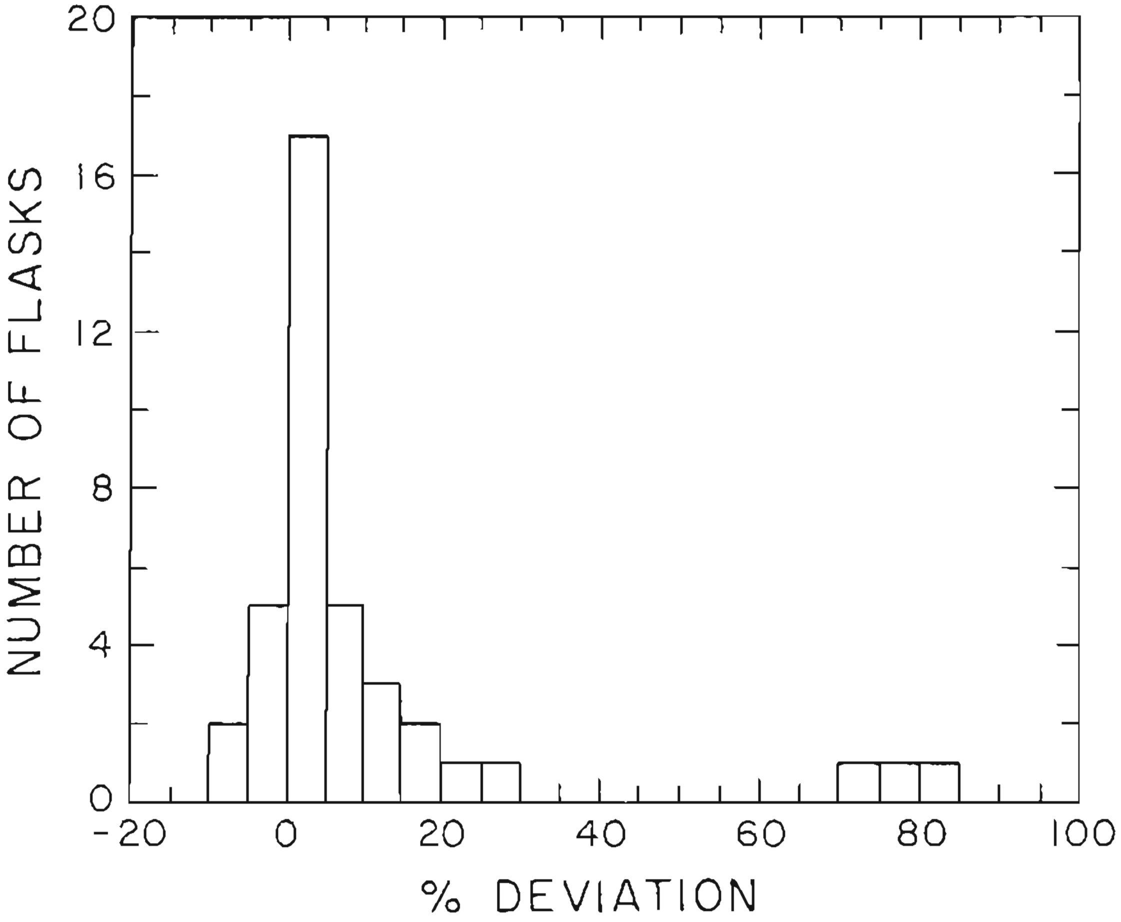


FIGURE 3.B.3: Long Term Stability of CH_3Cl in Small Sampling Flasks. The concentration of 1 of the flasks deviated by more than 100% after long term storage and is not shown in this histogram.

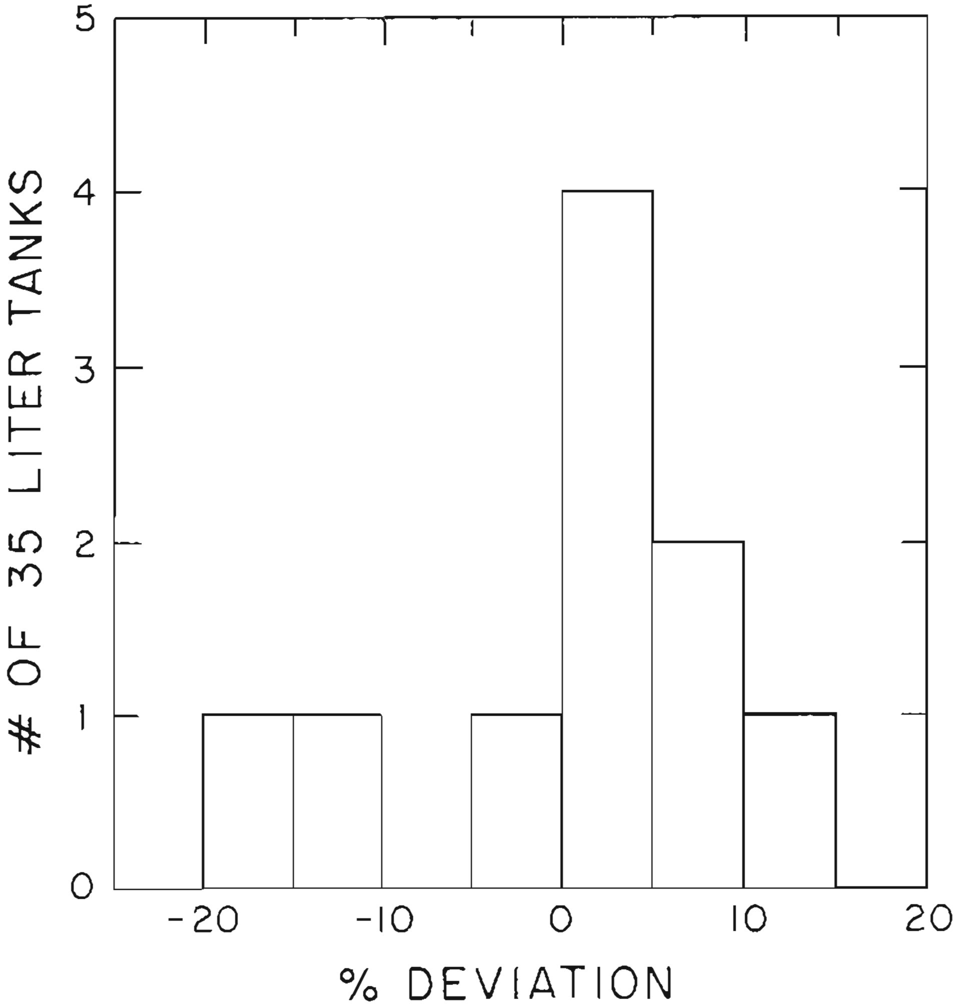


FIGURE 3.B.4: Short Term Stability of CH_3Cl in 35 L Sampling Tanks.

3.C. Particle Collection and Analysis and Light Scattering Measurements

Suspended particles were collected on Teflon filters by an EPA cyclone sampler and on quartz filters by an impactor. The EPA cyclone sampler was designed to meet the specifications of John et al., 1980 with a flow rate of 25 L/min to remove particles with aerodynamic diameter of 2.5 μm or above from the flow stream. The single stage impactor was built at the Oregon Graduate Center and also calibrated with a cutpoint of 2.5 μm. Flow rates were measured before and after each exposure of a filter with a rotameter, which was calibrated against a dry test meter on a periodic basis.

The filters were weighed twice each before and after exposure on a Cahn 25 electrobalance. The calibration of the electrobalance remained within ±1 μg over the period of filter weighing and the standard deviation of repeated weighing of the same filter was ±10 μg. Blank filters were taken to the field site and brought back without exposure to serve as a control on filter handling in the field. The weight of the blank filter never deviated more than 10 μg from the original weighing. The atmospheric concentration of fine particles over the sampling period was calculated as the mass of the fine aerosol divided by the volume of air sampled, which is the average flow over the sampling period multiplied by the sampling time.

A comparison between the atmospheric fine particle concentrations measured with the cyclone and the impactor was made during 7 periods of collocated sampling. This values are shown in Table 3.C.1. No statistical difference was found between the two measurements (paired t-test, $\alpha=0.05$).

The Teflon filters were analyzed by x-ray fluorescence on an ORTEC TEFA 6110 system with a dual Mo-W anode x-ray tube and .03 mm Mo and Cu foil filters and a 160 eV FWHM Si(Li) detector. The elemental analysis was performed under the procedures developed for the PACS project (Cooper, 1978). The quartz filters were analyzed by a thermo-optical method (Huntzicker et al., 1982, and Johnson et al., 1981) for organic and elemental carbon.

An MRI 1550 integrating nephelometer was used to measure the light scattering coefficient (b_{scat}). The instrument was calibrated as suggested by Ruby and Waggoner, 1981, with a zero point using filtered air and an upper range point using the known scattering coefficient for Freon-12. The zero and span of the instrument were checked on a weekly basis. A plot of measured mass using the cyclone sampler and b_{scat} is shown in Figure 3.C.1. The correlation coefficient is r=0.94 with 90% confidence limits that r lies between

0.88 and 0.97 (Fisher Z Transform). The relationship between b_{scat} and fine particle mass is $b_{scat}(10^{-4}m^{-1}) = 0.29 \pm 0.17 + 0.046 \pm 0.003(\text{mass})(\mu g/m^3)$ compared with the relationship found previously in the PACS study for Portland by Shah et al., 1985: $b_{scat}(10^{-4}m^{-1}) = 0.13 + 0.046 \pm 0.001(\text{mass})(\mu g/m^3)$. The intercept represents the Rayleigh scattering coefficient, which is about 0.21 at the elevation of the study (Ruby and Waggoner, 1981) and the slope demonstrates the relationship between light scattering and the Portland fine aerosol. The agreement between the two studies for the value of the slope validates the accuracy of the aerosol and scattering coefficient measurements.

In the next chapter the experimental data will be applied to estimate local pollution from woodburning in and around Portland, Oregon.

Table 3.C.1

Date	Sample Period	Measured Fine Particle Concentration (d < 2.5 m) $\mu g/m^3$	
		Impactor	Cyclone
1/17/84	12 hour	70	67
1/19/84	12 hour	46	56
1/26/84	12 hour	50	48
1/31/84	12 hour	90	106
2/3/84	12 hour	60	52
2/6/84	6 hour	83	82
2/7/84	6 hour	37	37

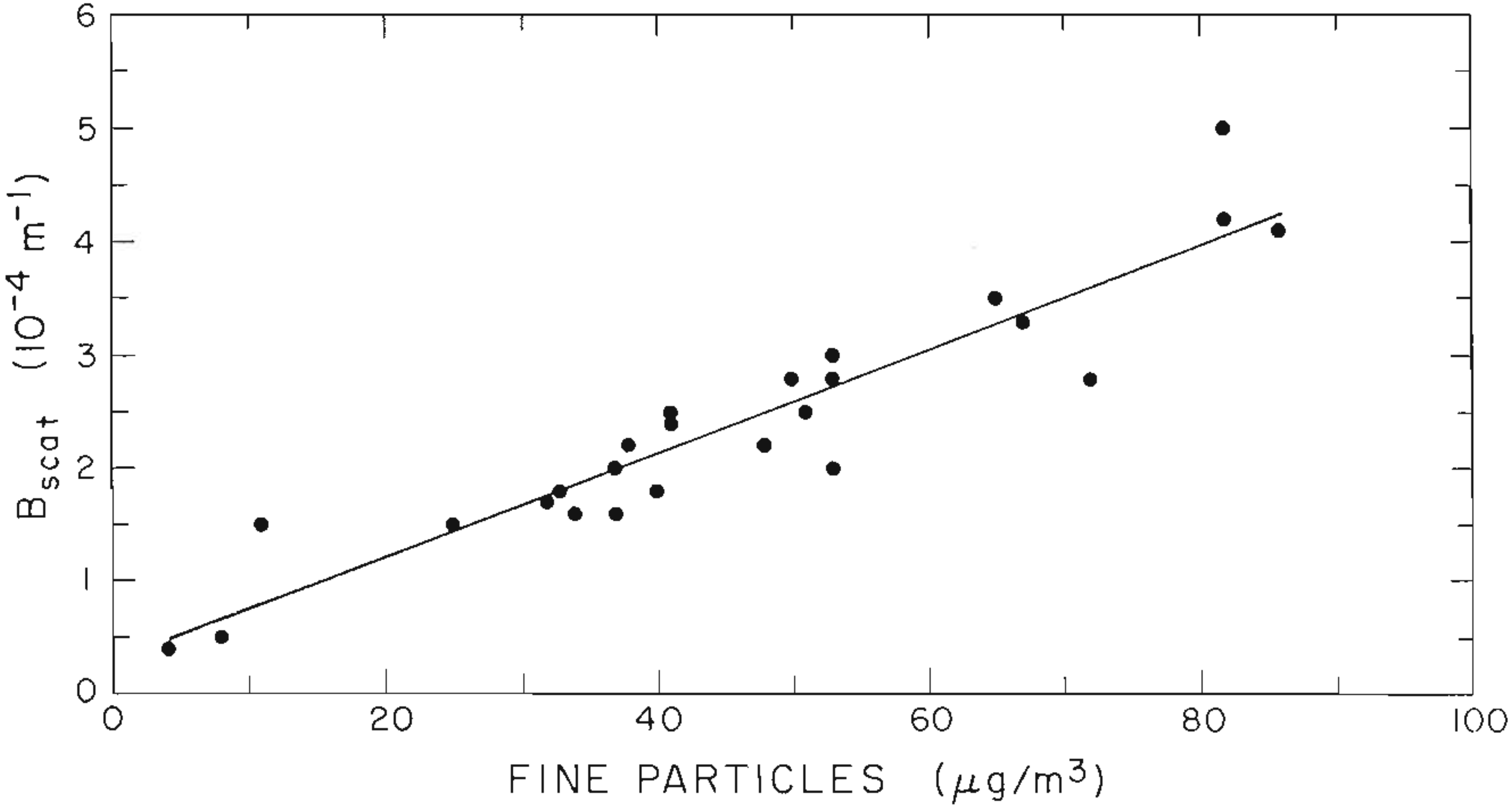


FIGURE 3.C.1: Light Scattering Coefficient versus Fine Particle Concentrations in Hillsboro

CHAPTER 4

MODEL RESULTS: Estimation of Wood Combustion Contribution to Local and Regional Fine Particulate Pollution using the Methyl Chloride Tracer Approach

4.A Development of Source Emission Factors for Aerosol/CH_3Cl Ratios

A study was conducted to experimentally measure the ratio of gaseous CH_3Cl to fine particle mass in woodsmoke for application in the methyl chloride tracer approach and in the chemical mass balance effective variance receptor model. Samples were collected from the cooled diluted plume from home chimneys to approximate as closely as possible the actual conditions of woodsmoke as it enters and becomes dispersed in the urban atmosphere. A portion of the plume was drawn into a dilution chamber with a residence time in the chamber on the order of 2 to 3 minutes. Carbon dioxide measurements in the flue gas and in the sampled air indicated that the dilution factor was from 50 to 150 during the test runs. A schematic of the sampling apparatus is shown in Figure 4.A.1. The sample was drawn from the dilution chamber through an in-line filter by a bellows pump and into an evacuated cylinder. The cylinder was taken to the laboratory for analysis of volatile components in the woodsmoke plume. Particulate samples were also collected by a parallel set of impactors to determine the size distribution of the particles. These samples were analyzed for organic and elemental carbon and for elemental species by X-ray Fluorescence (Rau and Huntzicker, 1985 and Rau, 1985).

The source sampling experimental design was based on a stratified sampling scheme incorporating burn conditions and wood types typical of the Portland, Oregon area. The test woods included local varieties of fir, alder and oak. Three different box style wood stoves, three different fireplace inserts and three different fireplaces were tested under the damper open condition and the damper all or partially closed condition. The damper open condition corresponds to a hot burn at a firebox temperature of around 500-600°C. The damper closed conditions corresponds to a cool burn and firebox temperature of 250-300°C. The burn rate of the wood which can be controlled by the positioning of the damper has been demonstrated to be one of the most important factors determining the chemical characteristics and emission per unit time of aerosol from wood burning stoves (Oregon Department of Environmental Quality, 1981; Muhlbaier, 1981; Barnett, 1981; Cooke et al., 1981; Hubble et al., 1981).

Similar procedures for startup of the fire were carried out during each experiment. Integrated samples of dilute woodsmoke were collected over twenty minute periods and analyzed for CH_3Cl, CO, CH_4 and other hydrocarbon gases. The sampling began 5 to 10 minutes after the startup of the fire. While the emissions may be higher during the initial startup, these conditions are not representative of the majority of the burn cycle and therefore were not included in the calculations of the gas concentration ratios. The emission ratios, $\alpha = Q_{aerosol}/Q_{gas}$, which are used in the model and discussed in Chapter 2, are presented in Table 4.A.1. A significant difference is found between the hot and cool burn of fir (Wilcoxon 2 sample test, $\gamma = 0.05$; Snedecor and Cochran, 1980; γ is used in this section to denote the significance level rather than the generally used α to avoid confusion with the source emission ratio, α) but no significant difference is found between the values for in the fir, damper open, the hardwood, damper open and closed, and the fireplace (Wilcoxon 2 sample test, $\gamma = 0.05$). Since fir and other softwoods generally have a higher content of wood extractives, it is not surprising to find considerably more condensible organic material, and therefore higher particle emissions, occurring under starved oxygen conditions during the burning of fir.

The emission ratios α are used in a stratified sampling scheme to predict the aerosol concentrations in the air from woodsmoke using the gaseous tracer CH_3Cl. The Oregon Department of Environmental Quality in 1981 surveyed 1108 households in the Portland area and found that 37% of the wood burned was burned in fireplaces, and for those who burn in wood stoves 19% of the population generally burn with an open damper while 81% burn with the damper partially or completely closed. The survey also estimates the number of woodstoves, fireplaces and fireplace inserts in use and the type of wood generally used. A weighting scheme is applied according to the percentages of the population burning under each condition to construct a composite α, α_{comp} for the Portland area.

The filter data from the source sampling experiments with similar dilution factors enables an approximate estimate to be made of the fine particulate mass contribution weighting factor relative to the softwood, cool burn for the other burn experiments. For example the hardwood, cool burn fine particulate emission factor is only 42% of the emission factor for softwood, cool burn. The contribution of each burn category to the composite α is determined by multiplying the percentage of the population burning in each burn category i, for example hardwood, cool, by the appropriate mass weighting factor and normalizing the sum of the percent contribution from all the categories such that $\sum_i p_i = 1$. This is shown in Table 4.A.2. Then the mean value of α_{comp} and its uncertainty can be determined using the stratified sampling statistics procedure as outlined by Hoel, 1971, by breaking down the variation in a variable into components to reduce the overall estimate of the uncertainties. If a population can be divided into k subpopulations, the mean and variance of each subpopulation can be determined separately. The mean value, μ, for the population is:

$$\mu = p_1\mu_1 + p_2\mu_2 + \ldots + p_i\mu_i \qquad (4.A.1)$$

where p is the probability that the random variable will lie in the i^{th} subpopulation. The variance of the mean in a stratified sampling system is:

$$\sigma_{\bar{X}}^2 = 1/n \sum_i^k p_i[\sigma_i^2 + (\mu_i - \mu)^2]. \quad (4.A.2)$$

where $\bar{X}$ is the estimated mean value, μ is the population mean and μ_i is the mean of category i and n is the sample size.

Since there was no statistically significant difference found between the average values of α for fireplace, hot and cool hardwood and hot softwood burning, the individual values for these types of burns are averaged together to give:

$$\alpha_f \ (10^2 \text{ g/g}) \ (\text{fireplace; stove burning hardwood hot and cool; softwood hot}) = 1.5 \pm 0.8 \ . \qquad (4.A.3)$$

Therefore two populations are used to determine the value for α_{comp}, the softwood cool burn and the α_f given above. Using the survey results, α_{comp} would be calculated as follows:

$$\alpha_{comp} \ (10^2 \text{ g/g}) = .65 \ (4.1) + .35 \ (1.5) \qquad (4.A.4)$$

where 65% of the mass is contributed from softwood, cool burning, and 35% is contributed from all other categories. The ratio α is multiplied by a conversion factor of 2.26×10^{-3} (μg/m^3)/pptv CH_3Cl for easy application of the model. The value for the emission ratio α_{comp}, applying a 5% (±1%) correction for the fraction of large particles (< 2.5 μm) found in the smoke samples, and the uncertainty of the ratio using the survey results to estimate wood type usage and typical burn conditions for the Portland, Oregon area is:

$$\alpha_{comp} \ (\mu\text{g/m}^3)/\text{pptv} = 0.68 \pm 0.13 \qquad (4.A.5)$$

where the ± value indicates the 95% confidence limits. It is important to note that knowledge of the woodtypes and burn conditions which are used in a community are necessary information for determining the appropriate local value of α_{comp}. However, with a small change in the percentages of the population burning with open or closed dampers, or with hard or soft wood, α_{comp} remains within the 95% confidence limits. Values for α_{comp} in $(\mu g/m^3)$/pptv are given in Table 4.A.3 assuming 40, 50 and 60% softwood burning and 60 and 81% cool burning.

Other gases analyzed in the smoke plumes were CH_4, CO, isoprene, α-pinene, benzene, toluene, ethylbenzene, m+p-xylene, and o-xylene. The average concentration ratios of these gases to carbon dioxide in the woodsmoke plume along with the concentration ratio of CH_3Cl is shown in Table 4.A.4. The emissions of the gases are reported in reference to the CO_2 emissions for comparison with other gas/CO_2 emission ratios which have been reported in biomass combustion (Crutzen et al., 1979; and Rasmussen et al., 1980b). The CH_3Cl to CO_2 ratio is significantly different between the fir, open damper and the fir, closed damper (Wilcoxon 2 sample test, $\gamma = 0.05$), while the ratio between the hardwood, open and closed damper is only marginally significant. There is no significant difference found between the hard and soft wood under the open and closed damper conditions (Wilcoxon, $\gamma = 0.05$). The ratio of CH_3Cl to CO_2 for the fireplaces is not significantly different from the fir, closed damper. The excess air and associated lower combustion temperatures in a fireplace may cause the increased CH_3Cl emissions. The differences between the ratios during the open and closed damper burns should be viewed with caution as the absolute emission rate of CO_2 during a cool burn with the closed damper may be reduced by a factor of 2 or 3 over that during a hot burn. Therefore increases in the gas/CO_2 ratio of less than 3 during a cool burn may be due to the decrease in CO_2 rather than the increase in the absolute emission rate of the gas itself.

Once the background value for CH_3Cl is determined, the value for α_{comp} given in Equation 4.A.5 may be used in Equation 2.B.6 to estimate the contribution of residential woodburning to local fine particle pollution. The background concentrations of CH_3Cl in the Portland area and globally will be discussed in the next section. Potential urban sources of CH_3Cl other than woodburning are reviewed.

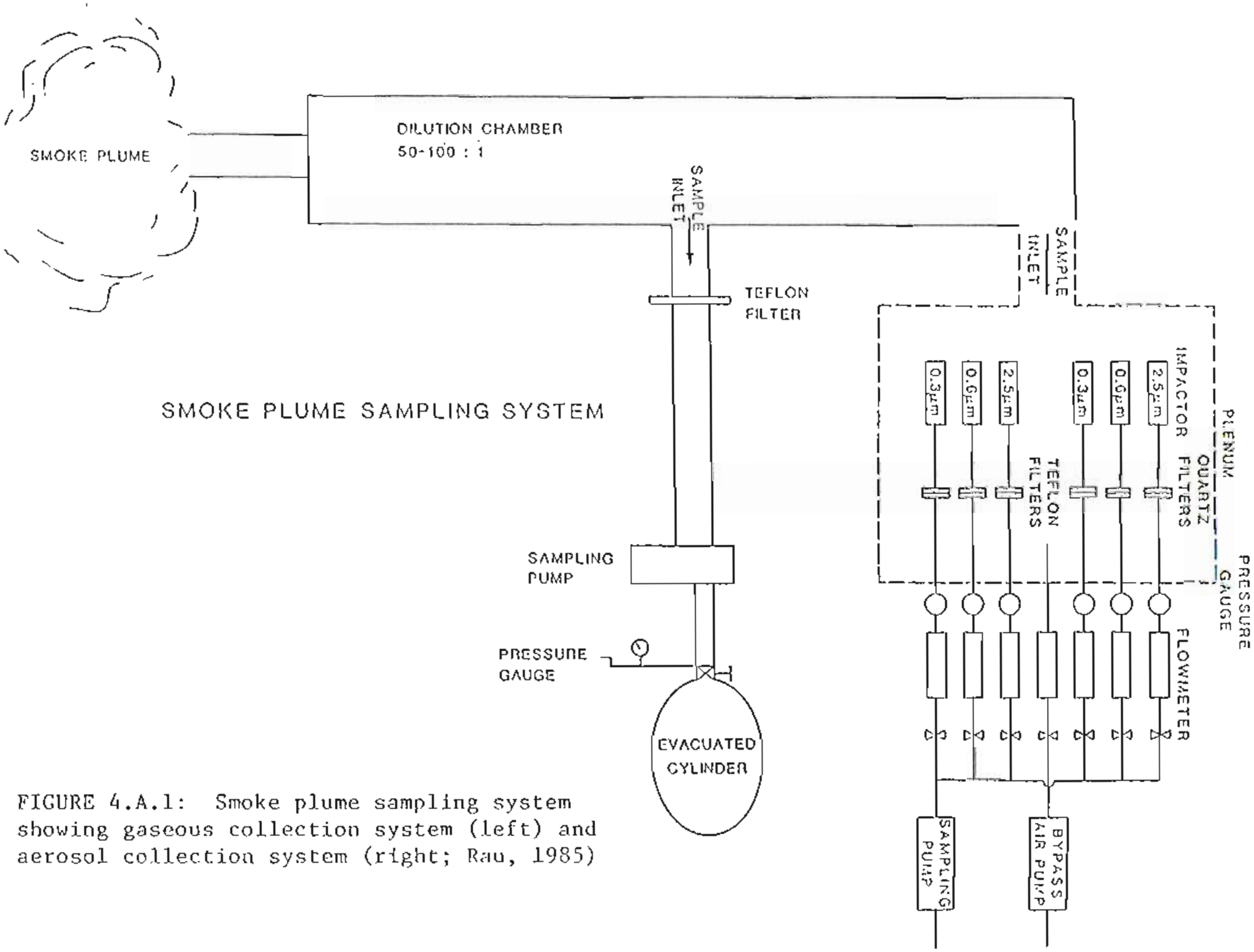


FIGURE 4.A.1: Smoke plume sampling system showing gaseous collection system (left) and aerosol collection system (right; Rau, 1985)

TABLE 4.A.1

Values for Source Emission Ratio, α, for Various Burn Conditions and Wood Types

	α (g/g) × 10^2	
Softwood, Fir	Open Damper	Closed Damper
Stove # 1	-	6.0
1	2.3	-
3	2.7	3.7
1	0.9	5.2
1	1.6	2.8
1	-	2.2
1	-	3.7
1	-	6.4
Insert# 3	1.8	3.0
Average ± Standard Deviation	1.9 ± 0.7	4.1 ± 1.6
Hardwood, Alder/Oak		
Stove # 1	0.3	1.2
1	0.7	1.6
1	1.9	-
1	1.4	1.4
2	1.9	1.9
1	1.0	0.6
1	0.9	0.9
3	-	2.5
Insert# 1	2.2	2.5
2	0.9	0.8
Average ± Standard Deviation	1.2 ± 0.6	1.5 ± 0.7
Fireplace, fir/alder/oak		
# 1	0.7	
1	0.4	
2	0.7	
1	1.4	
3	3.7	
Average ± Standard Deviation	1.4 ± 1.4	

TABLE 4.A.2

Burn Category i	% of Wood Burned in Each Category (10)*	Mass Emission Ratio Category i to Softwood Cool Category	Mass Weighting Factor	P_i
Softwood, cool	26	1.00	0.595	0.65
Softwood, hot	5	0.13	0.077	0.01
Hardwood, cool	26	0.42	0.250	0.27
Hardwood, hot	5	0.06	0.036	0.01
Fireplace	37	0.07	0.042	0.06

*assuming 50% of the wood burned is softwood and 50% is hardwood.

TABLE 4.A.3: Sensitivity of Composite Emission Ratio, α_{comp}, to Different Assumptions of the Percentages of the Population Burning Softwood and Hardwood and Hot and Cool Burn

$\alpha_{composite}$ ($\mu g/m^3$)/pptv

Percent Burning Cool	Percent Burning Softwood		
	40	50	60
60	0.61	0.65	0.69
81	0.63	0.68	0.72

TABLE 4.A.4

Average Gas/CO_2 Ratios in Woodsmoke Plume

	ppmv/ppmv			ppbC/ppmv						
	CH_3Cl/CO_2 x 10^{-5}	CH_4/CO_2	CO/CO_2	Isoprene/CO_2	α-pinene/CO_2	Benzene/CO_2	Toluene/CO_2	Ethyl-benzene/CO_2	m + p-xylene/CO_2	o-xylene/CO_2
Softwood, hot burn	1.39±0.45* n = 5	0.003±0.001 n = 4	0.055±0.018 n = 4	0.003±0.003 n = 3	0.003±0.003 n = 3	0.253±0.107 n = 5	0.190±0.071 n = 5	0.005±0.002 n = 5	0.009±0.002 n = 5	0.002±0.001 n = 5
Softwood, cool burn	2.65±0.72 n = 8	0.030±0.006 n = 6	0.223±0.066 n = 6	0.130±0.106 n = 3	0.233±0.100 n = 5	1.49 ± 0.58 n = 5	1.01 ±0.30 n = 5	0.097±0.030 n = 5	0.235±0.079 n = 5	0.080±0.029 n = 5
Hardwood, hot burn	0.66±0.11 n = 11	0.005±0.001 n = 10	0.065±0.012 n = 11	0.003±0.002 n = 3	0.007±0.002 n = 3	0.283±0.036 n = 9	0.071±0.021 n = 9	0.008±0.003 n = 9	0.013±0.006 n = 9	0.006±0.003 n = 9
Hardwood, cool burn	2.09±0.52 n = 9	0.017±0.005 n = 8	0.139±0.035 n = 7	0.094±0.052 n = 3	0.064±0.064 n = 3	0.740±0.188 n = 7	0.407±0.114 n = 7	0.052±0.016 n = 7	0.114±0.039 n = 7	0.042±0.013 n = 7
Fireplace	2.63±0.95 n = 5	0.005±0.001 n = 5	0.058±0.010 n = 5	0.015±0.011 n = 2	0.069±0.046 n = 4	0.493±0.271 n = 4	0.217±0.083 n = 4	0.024±0.013 n = 4	0.046±0.019 n = 4	0.011±0.003 n = 4

* ± values are standard error of mean

4.B Background Analysis of Tracer Species

If a tracer species has a known nonurban source which contributes to a background concentration of the species, that concentration must be well characterized. The uncertainties of the background concentration must be propagated to the uncertainty of the receptor model estimate of the urban source contribution. If there are major local sources of the species other than the source of interest, it will be necessary to use a multicomponent mass balance model. If there are no other significant sources of the gas, the unique gaseous tracer approach may be used if the urban background concentration of the gas can be determined. The background concentration at the receptor can be estimated during seasons or times of the day when the source emissions of interest are zero. If the tracer gas has a global background with a seasonal cycle, the background at the receptor may be estimated by the background at a nearby site where no local sources of the gas exist. This is the approach followed in the use of CH_3Cl to apportion the sources of residential woodburning in Portland, Oregon.

Ideally, measurements of the trace gas in the upwind rural sector of the urban area to be characterized may be made to estimate the background concentration, C_{io}, in equation 2.B.6 at the urban receptor. Variations within that sector represent the expected uncertainty in C_{io} . Because continuous measurements within the upwind sectors are not practical, measurements of typical concentrations within a rural sector isolated from the urban plume as a function of time, season and meteorological conditions may be used to represent the urban background trace gas concentration. The uncertainty in C_{io} may be substantially greater for a gas which must be characterized in this manner than for one with a low backgound concentration. Meteorological parameters and unusual extra-urban source contributions are expected to cause the largest deviations in C_{io}.

In characterizing an area source such as residential woodburning, the rural emissions from the source must be considered. If the contribution from both rural and urban burning to urban pollution is to be characterized, then it might be more appropriate to use the global background concentration as C_{io}. In this case consideration of possible depletion of the aerosol due to wet or dry deposition, sedimentation amd diffusional loses must be taken into account. If it is only of interest to apportion the contribution of urban woodburning to the urban atmosphere then it is appropriate to use the rural background concentration as C_{io}. This is the approach taken in the next section of this dissertation.

Methyl chloride is the most abundant halocarbon in the earth's atmosphere. It was first measured in the atmosphere over Southern England and Ireland by Lovelock and Margulis, 1975, using an electron capture detector; and in the air over the United States by Grimsrud and Rasmussen, 1975, using a mass spectrometer. Its predominant source is from the marine environment and though it is used in industry as an intermediate, it is believed that very little is released to the atmosphere from industrial sources (Lovelock, 1975, 1977). Dispersive loses from industrial production (Little, 1975, 1978) are estimated to contribute only 3 pptv to the global methyl chloride concentration (Altshuller, 1980). Methyl chloride is produced by biosynthesis in fungal cultures, (Hutchinson, 1971; Cowan, 1973; and White, 1982), and it has also been suggested that methyl chloride may be produced in rotting wood, Lovelock, 1980. Vegetative burning is probably the largest non marine source of methyl chloride to the atmosphere (Palmer, 1976, Crutzen et al., 1979; Watson et al., 1980). In Table 4.B.1 the global and urban sources of methyl chloride are listed.

The background concentrations and seasonal cycle of CH_3Cl is well documented (Rasmussen et al., 1980, Khalil and Rasmussen, 1981). The regional background cyle used in this study is also documented

(Edgerton et al., 1984, Appendix A). In Figure 4.B.1 the seasonal cycle is shown for the background site chosen for this study, the Oregon Graduate Center (OGC), a several hundred acre site surrounded by low housing density, meteorologically isolated from the urban Portland plume and only 10 km from the nearby residential receptor site in Hillsboro, Oregon. A series of three samples collected daily show the estimated error of the mean to be about 2% of the measured background concentration. In Figure 4.B.2 the cycle at the OGC site is compared with the global cycle measured at Barrow, Alaska (Khalil and Rasmussen, 1985). The similarity in cycles and concentrations lends support to the assumption that there are no local sources of methyl chloride in the study area other than biomass burning. The day to day variations in methyl chloride at the background site are probably due to nearby rural woodburning sources. Since the rural emissions are assumed to be part of the urban background the value for C_{io} used in the application of the unique tracer approach in the next section is that of the morning concentration at the background site generally measured within 24 hours of the sample at the receptor site.

Other residential heating sources and automobiles were sampled for any possible contribution of methyl chloride but none were found. On three different days, samples were collected in a tunnel on a major road during rush hour and analyzed for CH_3Cl. On all three days there was no significant difference found between the CH_3Cl concentrations in the nearby neighborhood with very little traffic and the tunnel with heavy traffic (t test, $\alpha = 0.01$). Samples were also collected in flue pipes of residential oil and gas burning furnaces and no elevated CH_3Cl was found. Measurements of CH_3Cl in the plume of a coal burning power plant showed a slight decrease in the plume concentration over the ambient (Khalil, Rasmusen, Edgerton, unpublished data). It is concluded that automobiles, oil and gas residential heating furnaces and coal-fired power plants are not sources of CH_3Cl.

Because of the high temperatures in industrial hogged fuel boilers methyl chloride is not expected to be produced there. A boiler was sampled which was burning at low efficiency and lower than normal temperatures and therefore representative of the maximum CH_3Cl emission expected from this source. The value for the CH_3Cl to CO_2 ratio found in the sampled boiler was on the order of 10^{-7} and the emission ratio for the aerosol to CO_2 was estimated by the company to be 2.4×10^{-2}. The CH_3Cl to particle ratio in hogged fuel boilers is therefore about one thousand times less than that found in woodstoves, a value too low to interfere with its use as a low temperature wood combustion tracer. The emission rate of CH_3Cl from the boiler is estimated to be about 10^{-4} the emission rate from woodstoves. Therefore the emissions of CH_3Cl from hogged fuel boilers are negligible compared to the woodburning emissions and do not need to be considered as a background source of CH_3Cl.

There are no municipal incinerators in the area but these generally also burn at high enough temperatures for the production of methyl chloride to be minimized. Occasional high background concentrations of CH_3Cl have been found in Lisbon, Houston, and L.A. by Singh et al. (1979, 1982) and these may be due to low temperature incinerators or nearby industry. In conclusion, no anthropogenic sources other than biomass burning were found to contribute to the elevated CH_3Cl concentrations in this study. However before this gas is used as a tracer elsewhere, the background sources should be investigated, as with all species in any receptor model.

The major sink of CH_3Cl in the atmosphere is its reaction with OH radicals. Khalil, 1979, estimates the global lifetime of methyl chloride to be 1-2 years. Therefore the gas may be assumed to be effectively inert over the times periods of interest in apportioning the daily contribution of woodburning to urban air pollution. Although methyl chloride is soluble in water, a simple calculation assuming equilibrium with raindrops shows that the amount of the gas dissolved in the rain is not of great enough quantity to measurably decrease the atmospheric concentration.

The uniqueness of methyl chloride to biomass burning sources, its relatively long lifetime and ease of measurement and its potential application in tracing woodsmoke on a real time basis make it an ideal gaseous tracer for use in receptor models. The high concentration of the global background of CH_3Cl compared to the typical ambient elevations during woodburning create a 20-30% uncertainty in apportioning the woodburning source. If a tracer could be found with a lower background, this uncertainty could be reduced. No such tracer was found that would have all of the ideal characteristics discussed above. The application of the unique gas tracer approach using methyl chloride to estimate the contribution of residential wood burning to urban air pollution is presented in the next section.

Table 4.B.1

Major Urban and Global Sources of Methyl Chloride

Global Sources	Reference
Marine (60-80%)*	Lovelock, 1975; Zafiriou, 1975
Fungal (?)	Hutchinson, 1971; Cowen, 1973; White, 1982
Biomass Combustion (10-25%)	Lovelock, 1975; Palmer, 1976; Crutzen et al., 1979; Watson et al., 1980; Rasmussen et al., 1980b

Urban Sources	Reference
Wood Stoves and Fireplaces	Khalil et al., 1983a; Edgerton et al., 1984
Backyard Burning	Edgerton et al., 1984
Building Fires	Palmer, 1976
Slash/Forest Fires	Stephens et al., 1969; Lovelock, 1975; Palmer, 1976; Crutzen et al., 1979; Watson et al., 1980; Rasmussen et al., 1980b; Tassio et al., 1984
Industrial Production of Silicones	Little, 1975, 1978; Altshuller, 1980

Urban Sources Tested for This Study Where No or Negligible Methyl Chloride Emissions Were Found:

Automobile
Oil Furnace
Gas Furnace
Hogged Fuel Boiler
Coal-Fired Power Plant

*Number in parentheses represents estimated source contribution to global methyl chloride budget

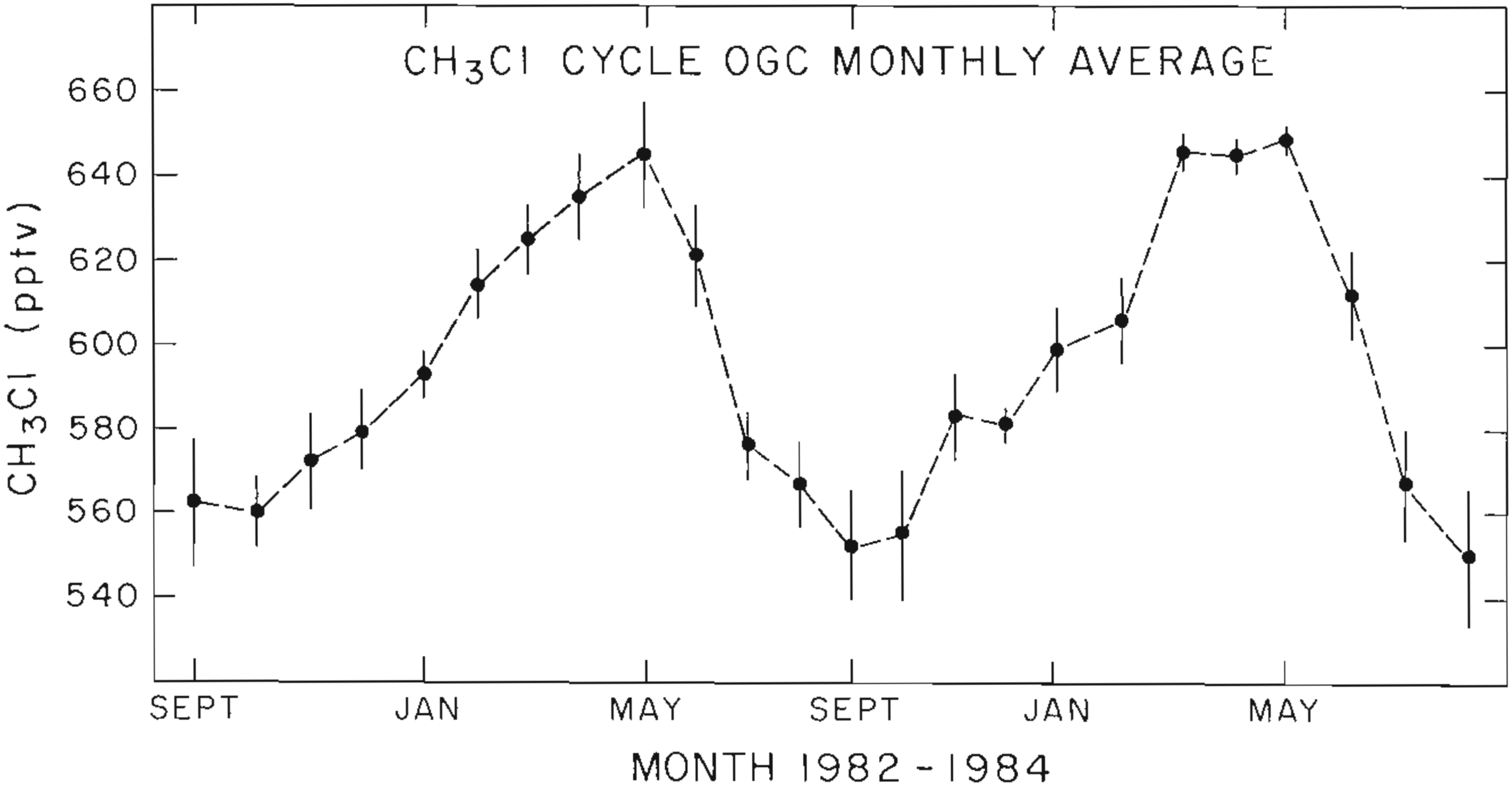


FIGURE 4.B.1: Cycle of CH_3Cl Concentrations at the Background Site, the Oregon Graduate Center (OGC)

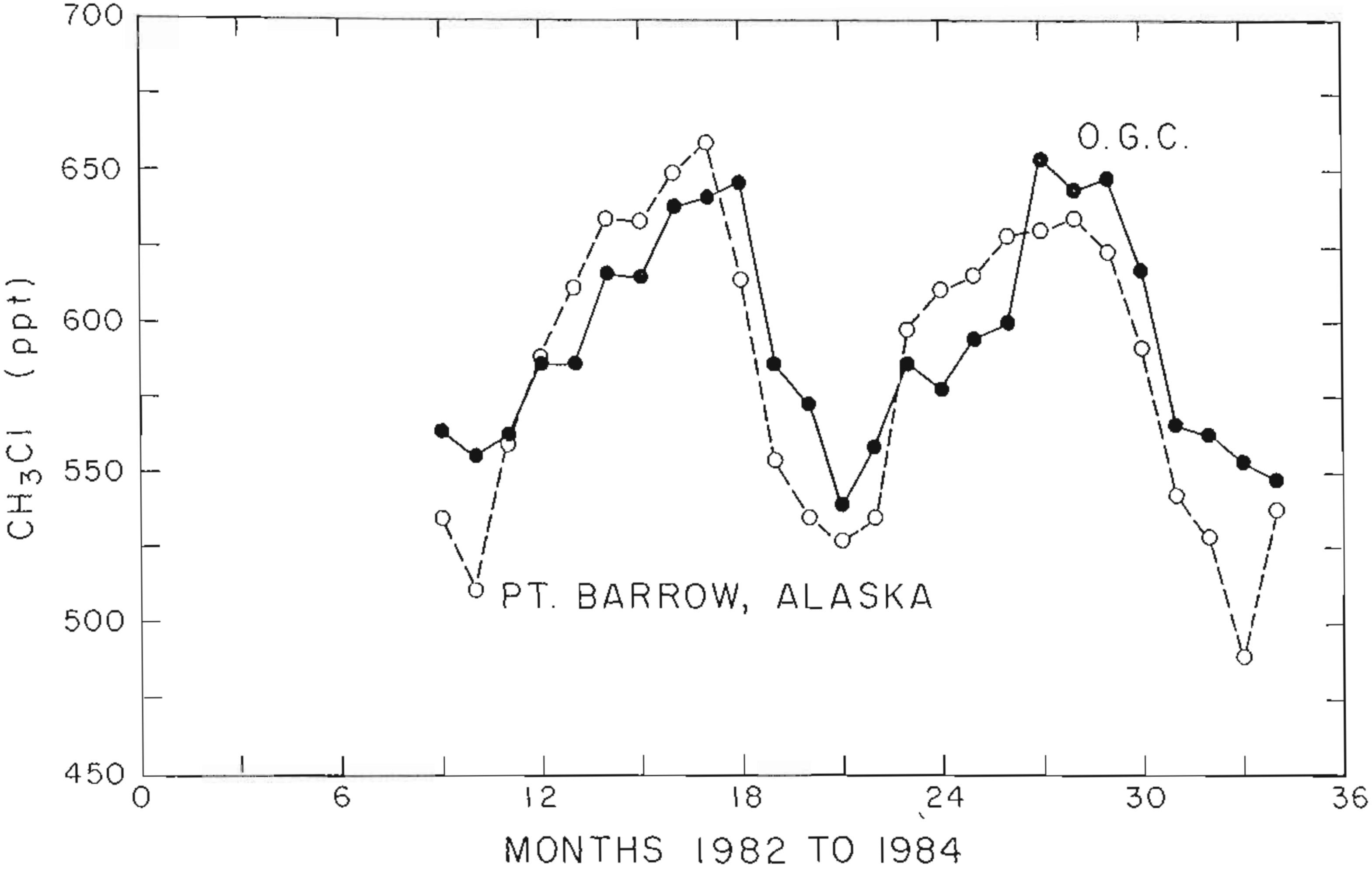


FIGURE 4.B.2: Comparison of the CH_3Cl Background Cycle at OGC and at Barrow, Alaska, from (Khalil and Rasmussen, 1985).

4.C Local Pollution from Woodburning

Gaseous air samples were collected from 1981 to 1984 in the Portland and Hillsboro, Oregon and analyzed for CH_3Cl to estimate the contribution of residential woodburning to urban air pollution. The background site throughout the study was chosen as discussed in the previous section to be the Oregon Graduate Center. The receptor sites included 4 residential neighborhoods. Site 1, in Hillsboro, Oregon was monitored for two years, beginning in September, 1982 and ending in June, 1984. Hillsboro is a small residential community about 25 kilometers from Portland. Local industry is limited to several electronics companies. The background site is only 10 kilometers from Site 1. Visual observation of smoke plumes from home chimneys confirms residential wood burning to be a major source of home heating in Hillsboro. Sites 2, 3 and 4 represent residential neighborhoods within the Portland city limits. Sampling was conducted at Sites 2 and 3 beginning in September 1982 and ending in October and July 1983 respectively. The major industries in the Portland area are metals production, manufacturing and shipping and the wood products industry. Site 2 is near the crest of a ridge following the Willamette River which runs through the city and Site 3 is located on terrain which gradually slopes toward the river valley. Higher winds are associated with Site 2. Site 4 was monitored September, 1983 through March, 1984 and represents a Portland neighborhood on a flatter terrain more isolated from the wind patterns of the River. Visual obervation of home chimneys at Site 4 also confirm the heavy use of wood for home heating. Figure 4.C.1 shows the location of the background and the receptor sites.

The average wintertime evening concentrations of aerosol ($\mu g/m^3$) from residential woodburning as calculated from the methyl chloride tracer approach, using a value for α of 0.6 ($\mu g/m^3$)/pptv, and the standard errors of the mean for all four receptor sites are shown in Table 4.C.1. The evening concentrations are represented by a grab sample collected at 9 PM. An integrated sampling system was also used over the winter of 1984 at Site 1. The system design and application are described in Appendix B (Edgerton et al., 1985). The lower concentrations of woodsmoke at Site 2 are due to the higher wind speeds and better meteorological dispersion. The highest concentrations of woodsmoke are found at Sites 1 and 4 due to the flat terrain, low winds and poor dispersion. Coincidental sampling was conducted at the sample sites in the evenings. No significant difference was found between the woodsmoke contributions at Sites 1 and 3 in 1982-1983 and between Site 2 and the background site during that winter (paired t-test, $\alpha = 0.05$). A significantly lower concentration was measured at Site 2 than at Site 1 or Site 3 ($\alpha = 0.05$). In 1983-1984, no significant difference was found between the woodsmoke contributions at Site 1 and Site 4 (paired t-test, $\alpha = 0.01$). On the average one could expect wintertime evening concentrations of fine particle pollution from woodburning stoves in Portland neighborhoods to be from 40 to 80 $\mu g/m^3$. Neighborhoods on hilltops and hillsides where windspeeds are likely to be greater, represented by Site 2, may experience very little buildup of pollutants from wood burning stoves.

The diurnal variation of concentrations of woodsmoke in the ambient air were also examined at Sites 1 and 4 (Edgerton et al., 1985b). Four samples per day were collected at Site 4, and 5 samples per day were collected at Site 1 every three days during the winter of 1984. High concentrations of fine particle mass, as calculated from the CH_3Cl tracer model, are found in the evening as expected when the emissions from wood stoves are the greatest. In Figure 4.C.2 the average concentrations of fine particles estimated from grab samples collected over the day are shown for Sites 1 and 4. At the Portland site (4), higher concentrations are observed during the day than at the Hillsboro site (1); however, concentrations remain high at Hillsboro in the late evening and early morning while they are reduced at Portland. Frequency diagrams of the concentration distribution of fine particles are shown in Figure 4.C.3 for grab samples at the Portland site and in Figure 4.C.4 for integrated samples at the Hillsboro site. As the averaging time for sample collection became shorter, the probability of detecting very high CH_3Cl concentrations increased. These high concentrations usually cannot be sustained for very long, and therefore the concentrations calculated from the grab samples may, on the average, be much larger than those calculated from the integrated samples. The frequency diagrams show that in Hillsboro the highest exposures may occur in the early morning, while in Portland they may occur in the early evenings. This difference arises from a number of causes, including the increased turbulence that is often found over the city due to the urban heat island effect, enabling better dispersion of pollutants in the early morning and preventing the polluant buildup that occurs in the surrounding suburbs.

A comparison of average fine particle pollution from woodburning over the wintertime in Hillsboro, as calculated from the model applied to the integrated samples, is shown in Figure 4.C.5 with estimated emissions over the day from a wood heat survey conducted by the Oregon Department of Environmental Quality (DEQ) to assess the times of day when most people burn wood. The survey area included Hillsboro. Again, it is evident that there is a discrepancy between early morning emissions and the modeled wood combustion contributions during that period. The occurrence of nocturnal inversions and low winds is common on winter evenings. The high concentrations during the early morning indicate that either little or no dispersion is occurring during this time and the early evening's accumulated pollutants remain in the air, or that many fires may still be smoldering and contributing to air pollution even though they are no longer tended. Finally, as an example of how concentrations of species associated with woodburning increase proportionately, the elevated evening concentration of CH_3Cl is shown along with elevated hourly values for CO and for the light scattering coefficient b_{scat} at Sites 1 and 4 on several days in Figure 4.C.6. By sampling and using source apportionment techniques over shorter intervals than 24 hours, high levels of short-term exposure may be identified. The extremely high concentrations that occur occasionally and are often sustained for 4 to 8 hours suggest that acute exposure to pollutants from residential woodburning may be of considerable importance. This issue is discussed further in Chapter 5.

Elevated concentrations of CH_3Cl from slash burning in the mountains 100 km from Portland were measured on one occasion on July 13, 1984, at a location less than 1 km from Site 2. The CH_3Cl concentration was elevated 117 $\pm$ 24 pptv indicating around 80 $\pm$ 16 $\mu g/m^3$ of fine particles in the air from slash burning. Nearby nephelometer measurements made by the Department of Environmental Quality registered a large increase on that day in the light scattering coefficient. A study of the use of methyl chloride as a tracer of pollution from slash burning on a regional scale was conducted at a remote site in a forested area 80 km east of Portland (Khalil et al., 1985b). Three events were noted over a period of about 5 weeks where there was evidence for low level longlived regional scale pollution as evidenced by excess levels of CH_3Cl and CO.

A two component CMB model was applied to estimate the portion of aerosol from autos and from wood stoves in Hillsboro on 8 mornings in the winter of 1984, using CH_3Cl and CO. If there are p source types contributing to the total aerosol mass which can be characterized by the measurement of n species, and p-1 source types emit unique tracer species, then the basic CMB equation reduces to the unique tracer characterization for the source types with the tracer species and a simple algebraic relationship for the remaining source type. This technique is called the tracer stripping method. In the two component model using CO and CH_3Cl to apportion woodburning and auto exhaust, the woodburning contribution is determined as described previously and the CO from woodburning is equal to $1/\alpha_{CO,WB}\ S_{WB}$, where $\alpha_{CO,WB}$ is the ratio of fine particle mass to CO in woodburning emissions. The remaining excess CO above the background concentration is attributed to auto exhaust and the contribution to the aerosol from auto exhaust is determined from $\alpha_{CO,Auto}$. A background concentration of 0.3 ppmv was determined for CO in Hillsboro from midday and early morning samples when there was little auto or woodburning contribution. The ratio of fine particulate mass to CO in auto exhaust, $\alpha_{CO,WB}$, is 47 $\mu g/m^3$ fine aerosol per ppmv CO was determined from the source tests of 4.A, and $\alpha_{CO,Auto} = 6.6$ ($\mu g/m^3$)/ ppmv CO (Metropolitan Service District estimate for Portland traffic). Propagating the errors in the estimates of $\alpha_{CO,Auto}$ and of the background CO concentration as described in Chapter 2.C, the uncertainty in the estimated auto contribution is about 40-50%. The results of the two component model suggest that the average concentration of fine particulate pollution from woodburning in the mornings in Hillsboro, 6-10 AM, is higher, but not significantly (paired t test, $\alpha = .05$) than the concentration of that from automobiles. While CO may be a useful tracer for auto exhaust in a small, isolated community like Hillsboro which has little industry, CO is emitted from most combustion sources and it would be difficult to use as a tracer in most cities.

Comparison of the expected concentrations of benzene and toluene from the wood combustion source emission ratios in Table 4.A.4 were made with those measured on 17 days in Hillsboro in the winter of 1984 when woodburning emissions accounted for 80-100% of the aerosol.

The results showed that wood stoves could account for on the average 35 ± 6% (90% confidence limits) of the ambient concentration of benzene but only 8 ± 2% of the ambient concentration of toluene. Wood stoves could account for a maximum of 8% of the ethylbenzene and 3-5% of the measured concentration of xylenes. No nighttime sources of isoprene are known except wood combustion, however this compound appears to be elevated on winter evenings above the concentration expected from woodburning. The variability in source emissions and the potential instability of isoprene in the source samples could cause the measured source ratios of isoprene to CO_2 to be lower than the ambient nighttime values from the burning of wood. The evening concentration ratios of benzene, toluene and isoprene to that of CH_3Cl are shown in Figure 4.C.7. This Figure suggests selective depletion of reactive species during periods when the ratios reach a minimum on January 26 and February 2, 4-7 and 9. An air stagnation advisory was posted by the National Weather Service during the first week in February and the temperature soundings indicate the presence of low level inversions on February 1,2, 4 and 7 corresponding to low points in Figure 4.C.7.

In the next section, the CH_3Cl unique tracer approach to estimating the contribution of residential woodburning to urban air pollution will be validated by comparing the results of this approach with the results of other methods of source apportionment applied concurrently.

TABLE 4.C.1

Average Evening Fine Particle Concentrations from Woodburning Estimated with the CH_3Cl Tracer Approach for Several Neighborhoods in Portland

	Average Fine Particle Concentration $\mu g/m^3$		
Receptor Site	Winter 1982-83 Grab Samples	Winter 1983-84 Grab Samples	Integrated Samples
Site 1 Hillsboro	73 ± 10* n = 24	67 ± 7 n = 28	50 ± 5 n = 27
Site 2 Alice Street, Portland	10 ± 5 n = 15	--	--
Site 3 Woodstock Blvd., Portland	37 ± 9 n = 19	--	--
Site 4 Lafayette St., Portland	--	68 ± 11 n = 31	--

* Standard error of the mean

TABLE 4.C.2

Contribution of Woodburning and Auto Exhaust to Morning Fine Particle Concentration in Hillsboro, Using a Two-Component CMB Model

Date	Morning Woodburning Contribution μg/m^3	Morning Automotive Contribution μg/m^3
2/27/84	3	11
3/2/84	13	9
3/4/84	62	2
3/5/84	0	13
3/8/84	28	12
3/9/84	40	2
3/22/84	0	4
3/23/84	16	0
	20 ± 8	7 ± 2

Average ± Standard Error

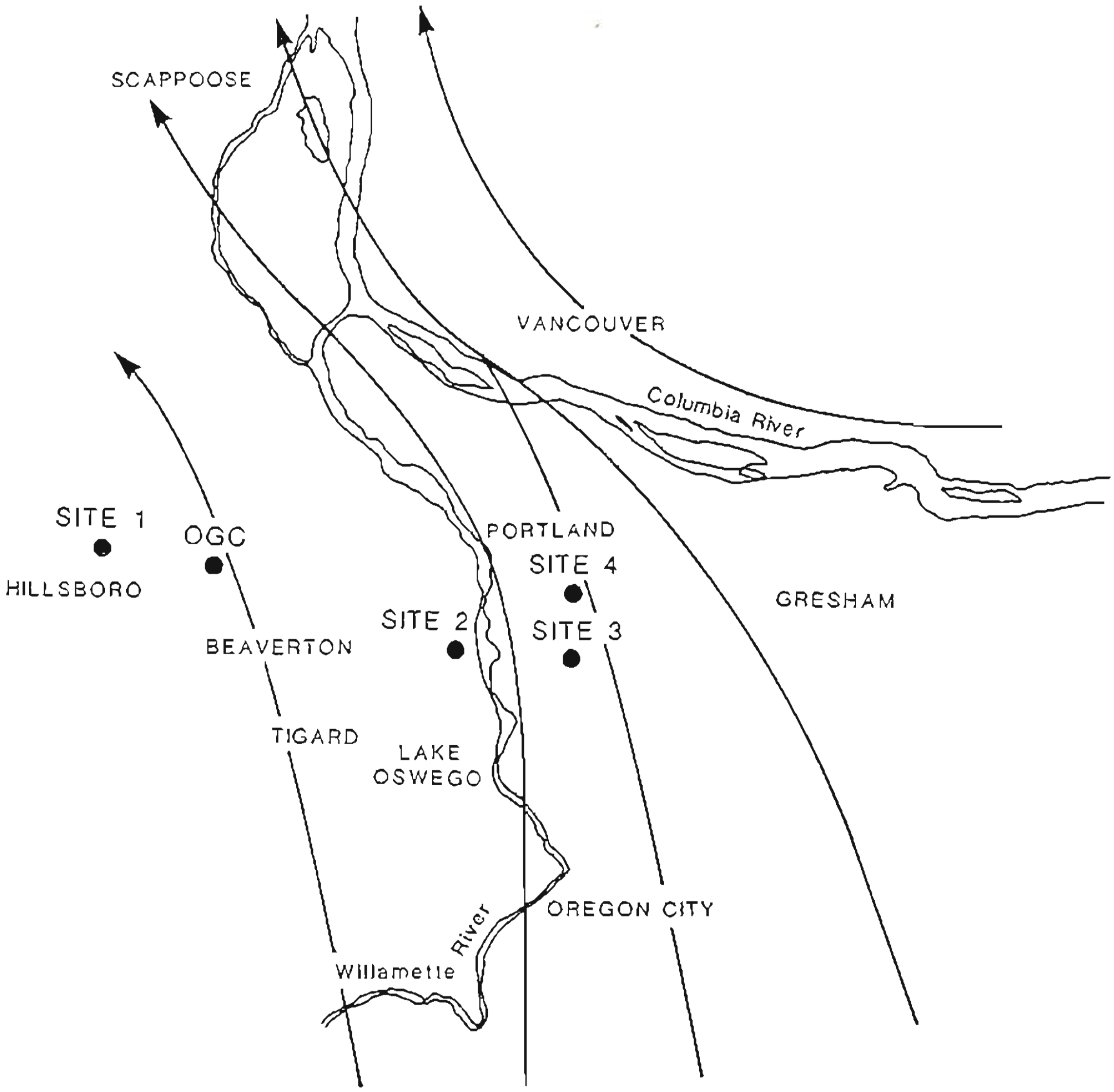


FIGURE 4.C.1: Map of Portland, Oregon Area Showing Sampling Sites and the Most Frequently Occuring Surface Wind Pattern in the Winter (Watson, 1979; Mathews, 1971; Cohen, 1977)

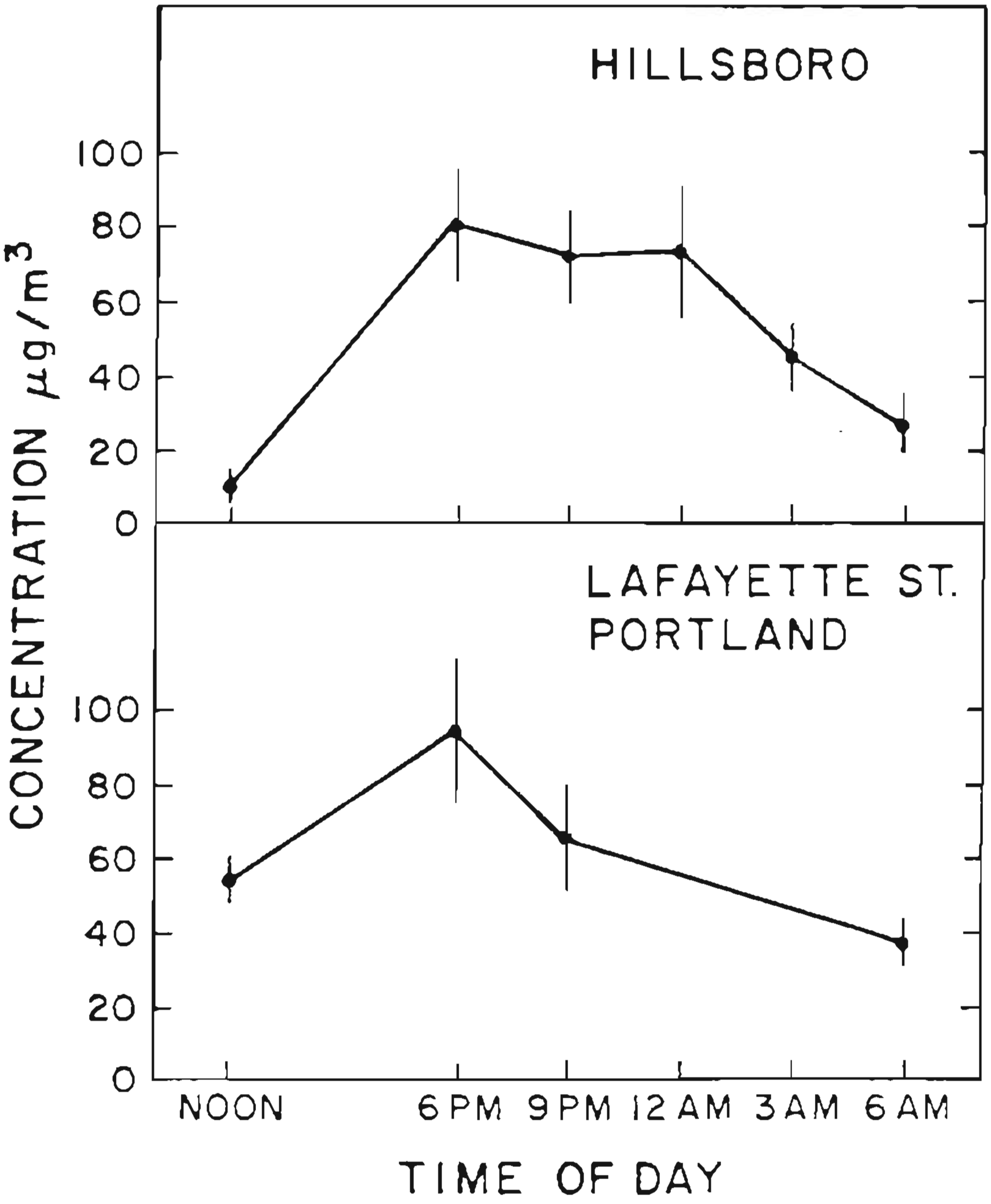


FIGURE 4.C.2: Fine Particle Concentration ($\mu g/m^3$) from Woodburning Calculated from the CH_3Cl Tracer Model in Hillsboro and Portland, Oregon, Showing Diurnal Variations. The concentration values are estimated from grab samples collected during late December, 1983 and January and February, 1984. The error bars denote the standard error of the mean for the samples collected. Each point represents 18-19 samples.

PORTLAND, OREGON

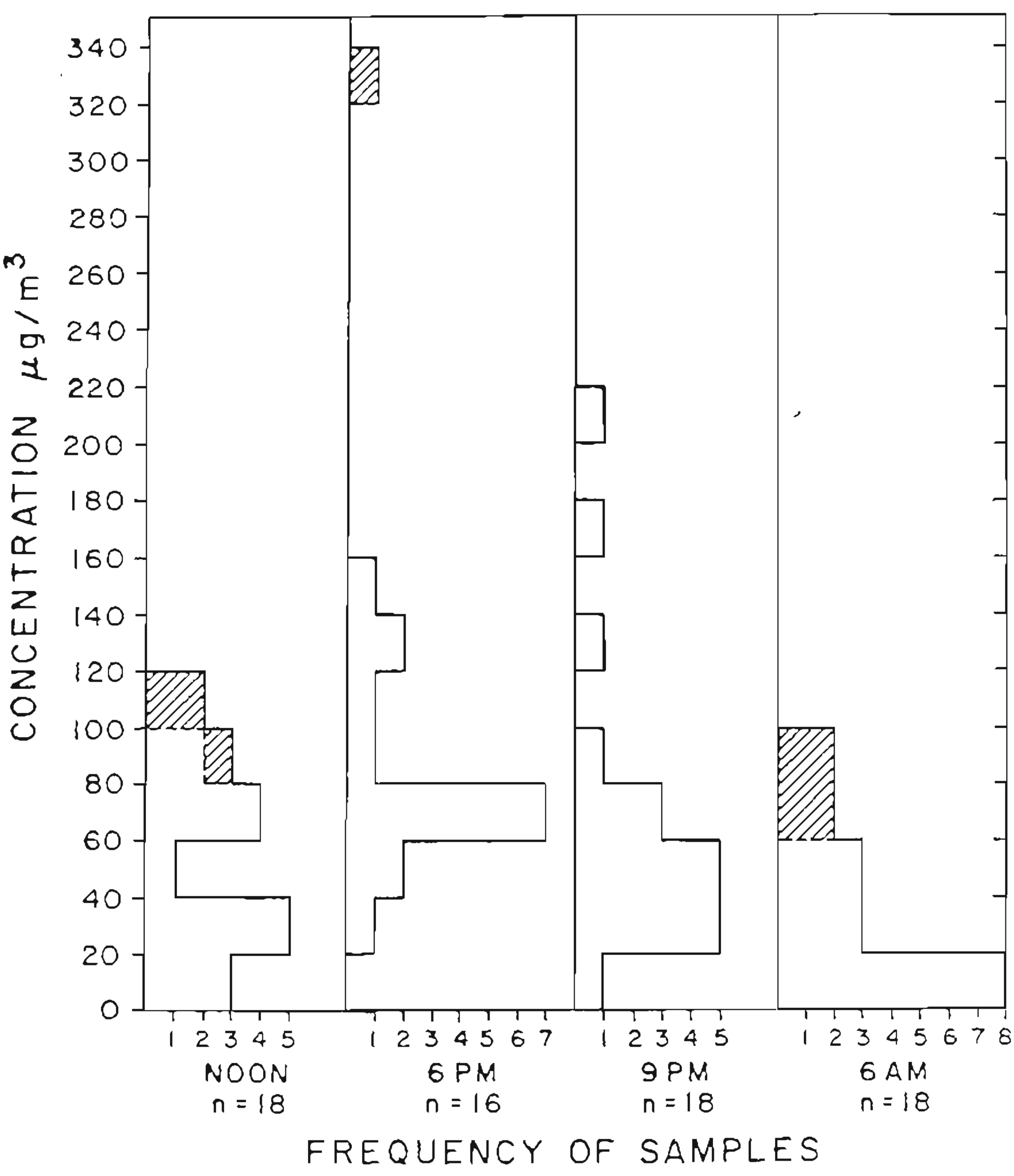


FIGURE 4.C.3: Frequency Distribution of Fine Particle Concentration (µg/m^3) from Woodburning in the Wintertime in Portland, Oregon. The fine particle concentrations were calculated from the CH_3Cl Tracer Model for grab samples collected at different times of the day. The dashed lines denote samples collected during foggy, stagnant meteorological conditions.

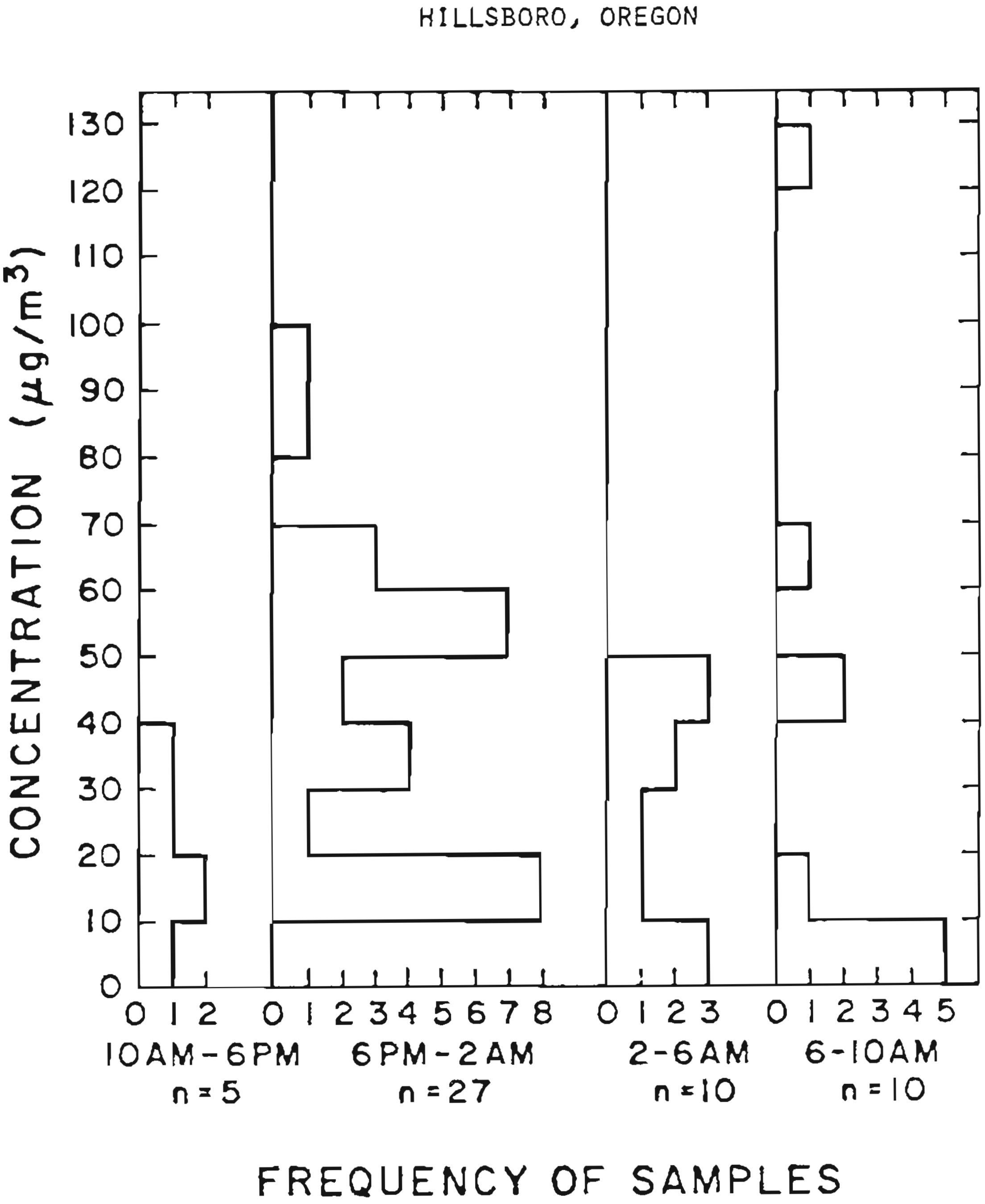


FIGURE 4.C.4: Frequency Distribution of Fine Particle Concentration ($\mu g/m^3$) from Woodburning in the Wintertime in Hillsboro, Oregon. The fine particle concentrations were calculated from the CH_3Cl tracer model for integrated samples collected over different periods of the day.

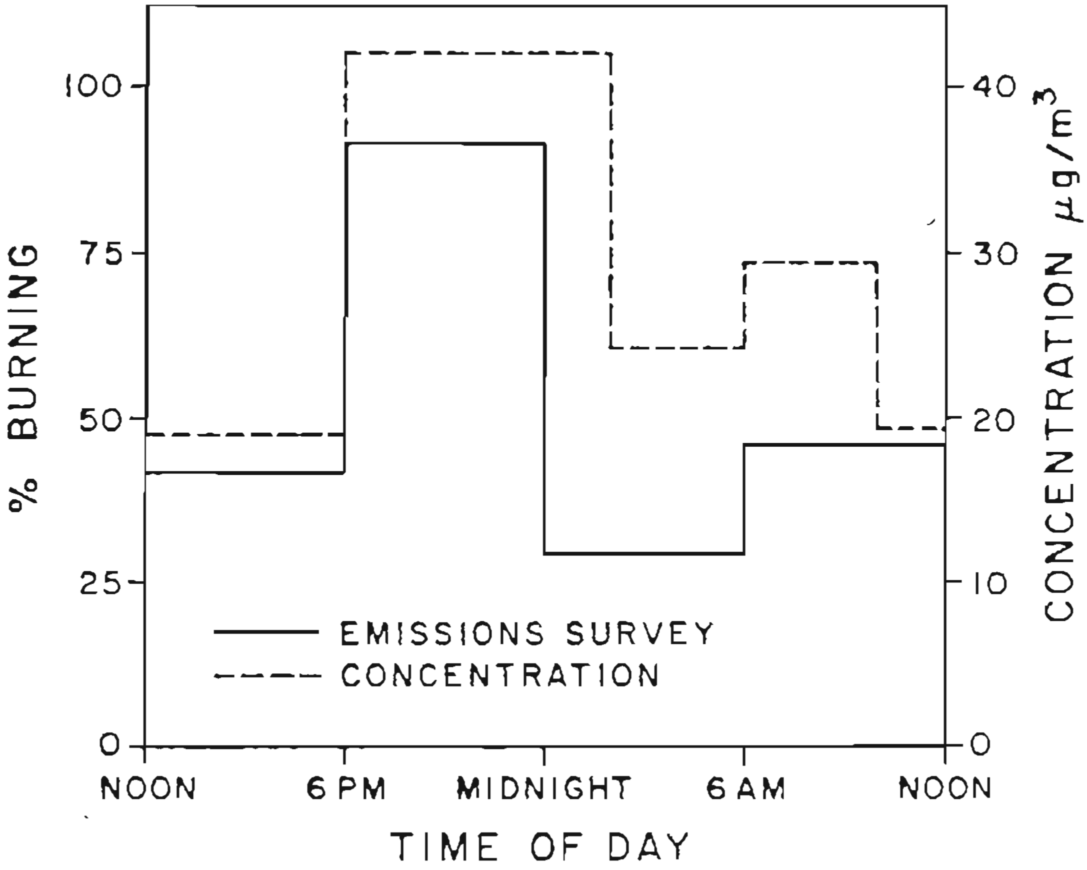
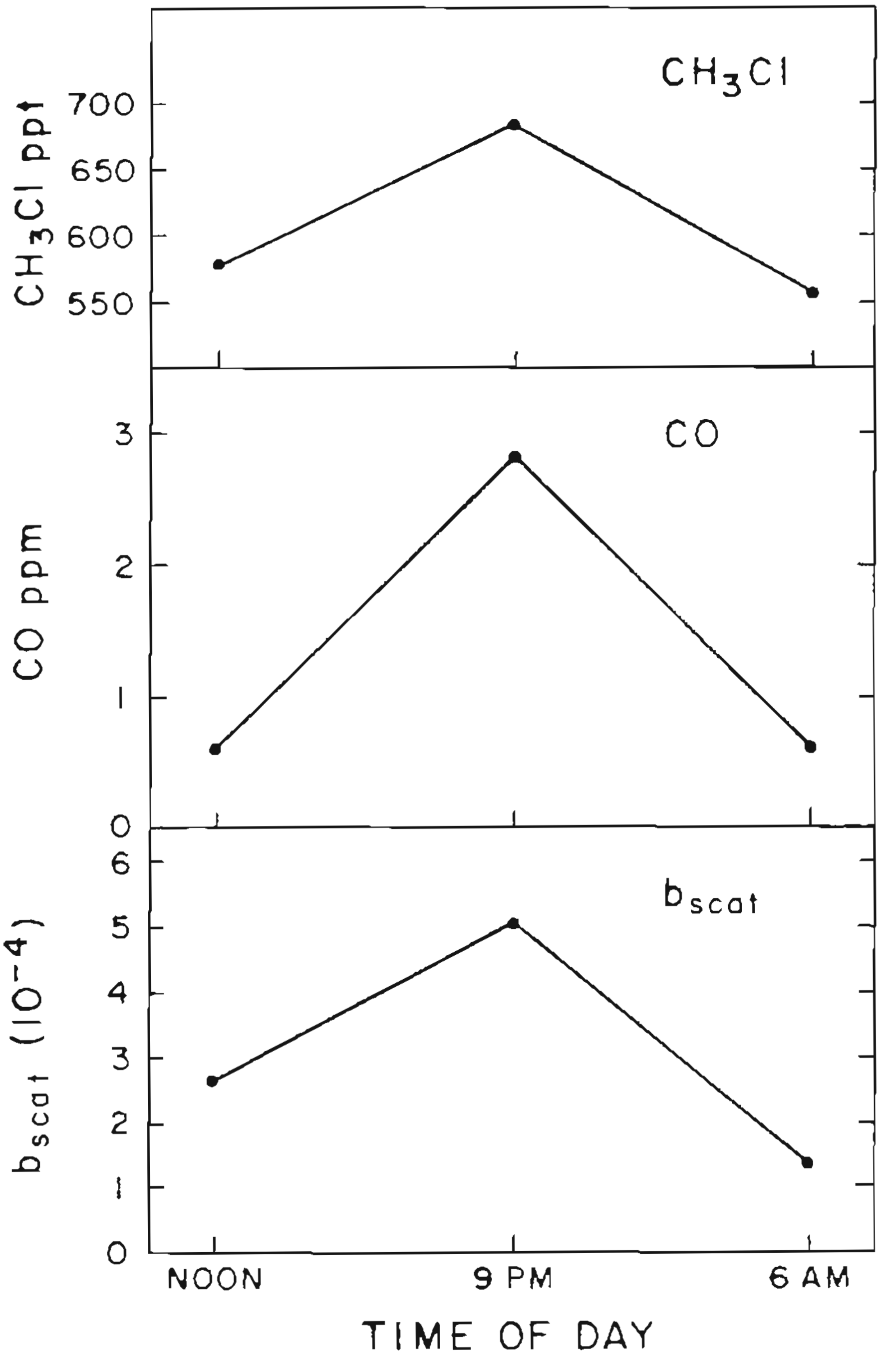


FIGURE 4.C.5: The Percentage of Woodstove Owners Burning During Different Periods of the Day in the Wintertime in in the Portland, Oregon area (DEQ Survey, 1982). Also shown is the average concentration of fine particles ($\mu g/m^3$) from woodburning during different times of the day in Hillsboro, Oregon which is included in the survey area. The concentrations during the early morning hours in Hillsboro are higher than the source emission estimates might predict.

PORTLAND, OREGON



FIGURES 4.C.6.i, ii, iii: Variations in the Concentrations of CH_3Cl, CO and the Light Scattering Coefficients, b_{scat}, Over the Day in Hillsboro for 10/10/83, 2/6/84, and for 1/16/84

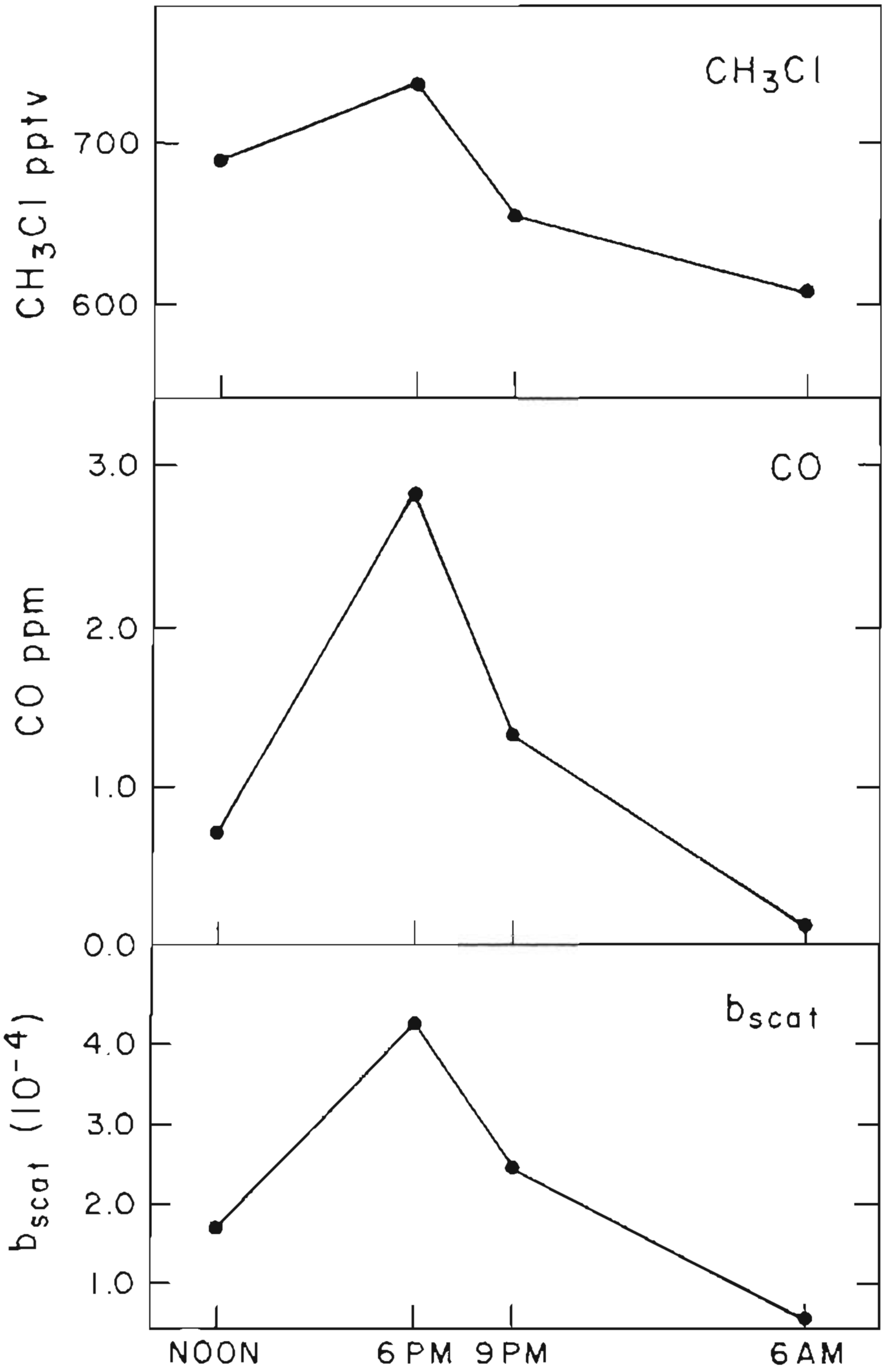


FIGURE 4.C.6.ii

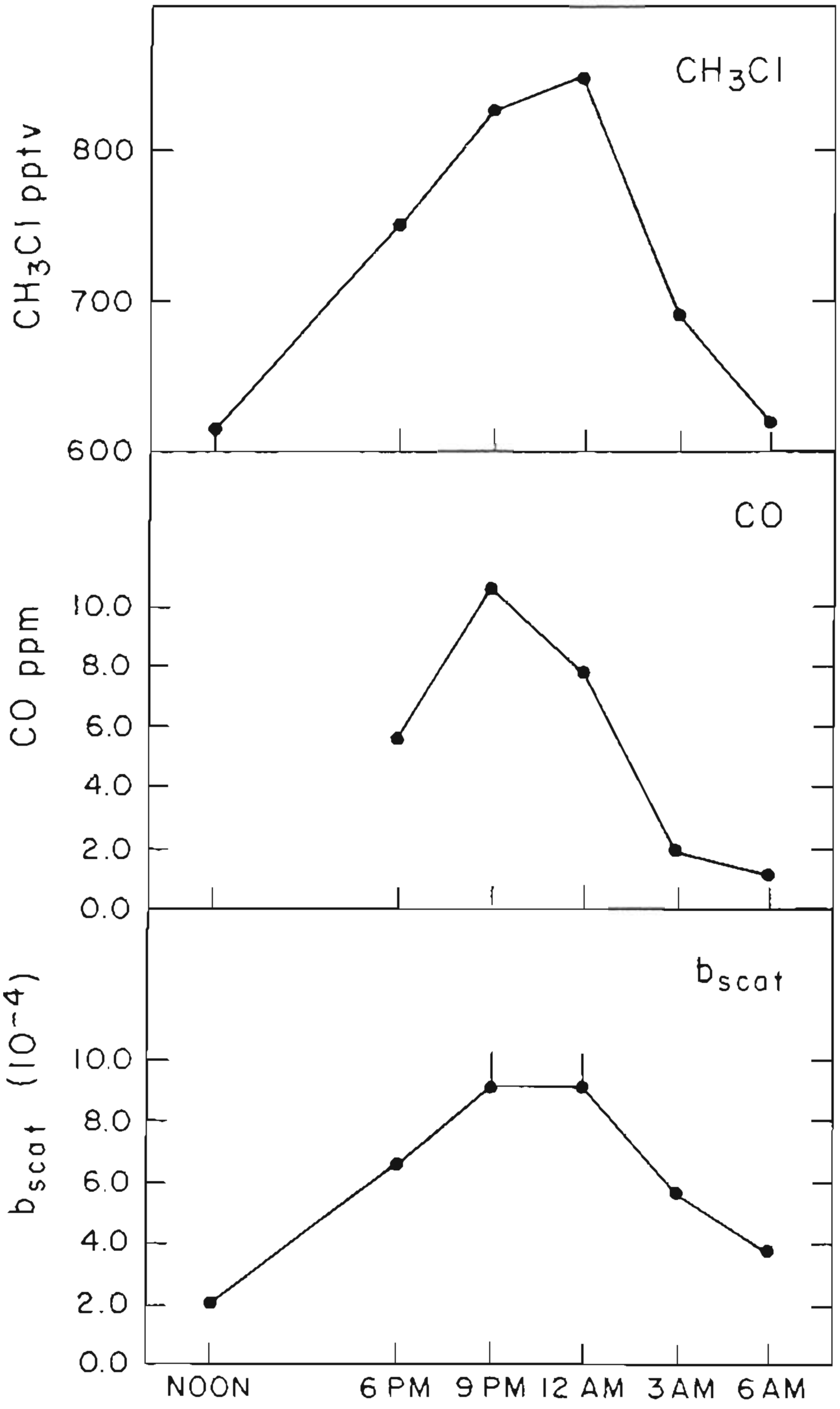


FIGURE 4.C.6.iii

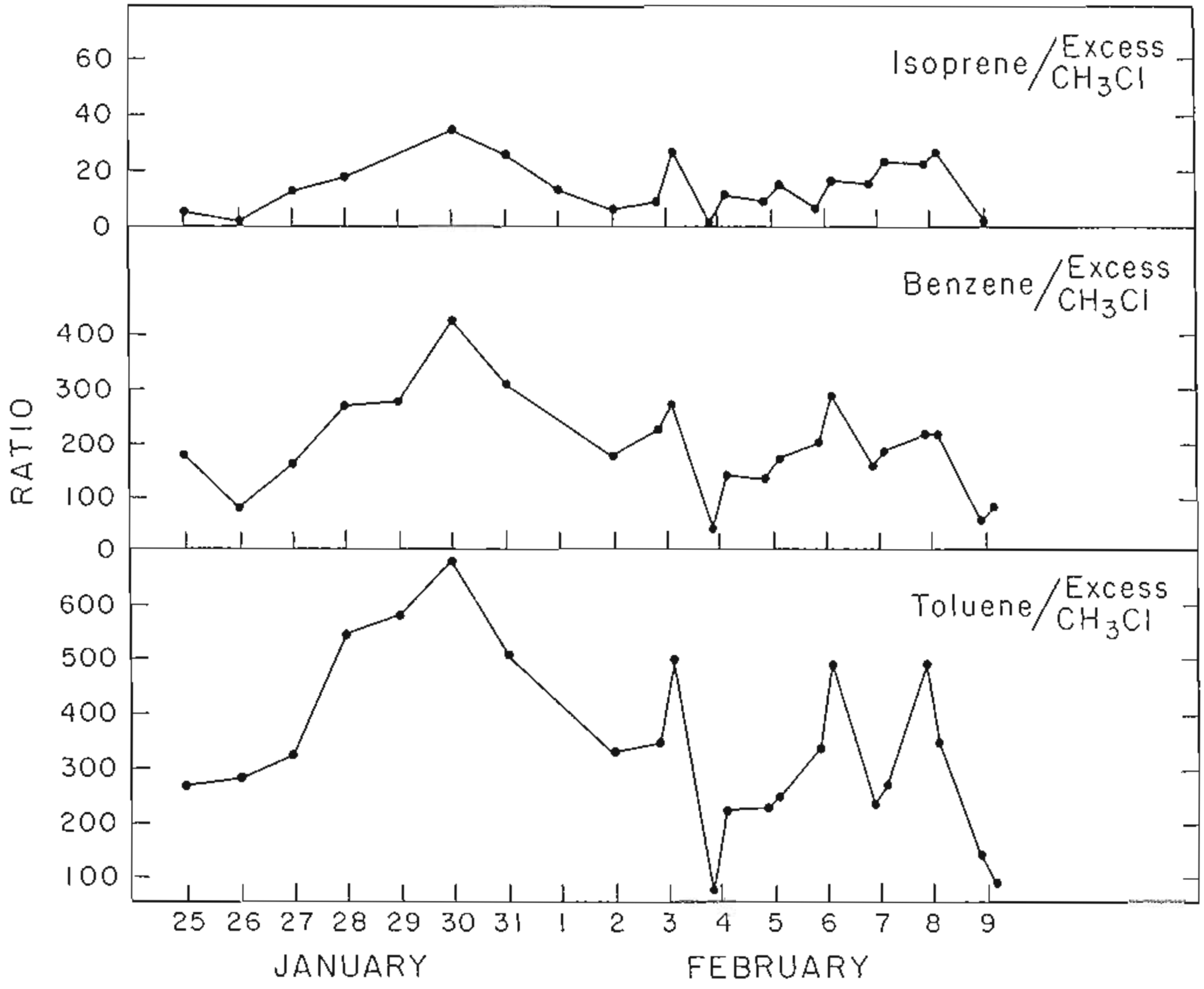


FIGURE 4.C.7: Ratios of Isoprene, Benzene and Toluene to Excess Methyl Chloride over a 15 Day Period in the Winter in Hillsboro, Oregon

4.D Validation of Methyl Chloride Tracer Approach to Estimating Fine Particulate Pollution from Woodburning

The precision of a model in apportioning sources of air pollution may be estimated from the uncertainties in the model parameters. The absolute accuracy of the model predictions, however, can not really be known. A common technique used to evaluate the validity of a model is to compare its results with those of other models. In this section the unique gaseous tracer approach to apportioning the contribution of residential woodburning to urban air pollution will be evaluated by comparing the consistency of the results using this approach with the results of other approaches. Wood combustion contributions to ambient fine particle concentrations derived from the CH_3Cl tracer will be made with (1) measured concentrations of fine particle mass and light scattering coefficients, (2) multicomponent Chemical Mass Balance calculations, and (3) box model estimates of the concentration of methyl chloride from woodburning.

Because there are few sources of fine particle pollution other than woodburning at Site 1 in Hillsboro, Oregon, a comparison of total fine particle mass should correlate well with fine particle mass from woodburning and therefore with the unique gaseous tracer of woodburning CH_3Cl. Figure 4.D.1 compares CH_3Cl measurements made over 4 to 12 hour periods in the evening with fine particle mass. Figures 4.D.2 shows the correlation between grab samples of ambient gases analyzed for CH_3Cl and with instantaneous measurements of the light scattering coefficient made in the evenings at Hillsboro. In Figure 4.D.3 the integrated CH_3Cl measurements over all periods of the day are compared with average light scattering coefficients during the sample periods and in Figure 4.D.4 the fine aerosol masses and the light scattering coefficients are compared. The correlation in both cases is significant, $r=0.67$, and 90% confidence that $0.44 < r < 0.82$ (Fisher Z Transform, Snedecor and Cochran, 1981). However the correlation is much better for the instantaneous measurements of CH_3Cl and b_{scat} ($r=0.8$ with 90% confidence $0.63 < r < 0.90$) which were conducted at peak woodburning times over only a few weeks (Khalil et al., 1983) shown in Figure 4.D.2 than for the comparisons of integrated samples collected during all times of the day. The variablility in the contribution from sources other than woodburning to fine particle mass and light scattering coefficient cause the correlation to be poorer during the longer sampling periods.

Gas and aerosol samples were collected concurrently on eight days for application in a chemical mass balance receptor model. The samples were collected over a 12 hour period during the evenings from 6 PM to 6 AM on four of the days, over a 6 hour period 6 PM to 12 AM on two of the days and over three hour periods on two of the days. On 2/3/84 only a 20 hour averaged carbon concentration was available and this was used to estimate the concentration during the 3 hour period over which the model was applied. The results of the comparison of model predictions are shown in Table 4.D.1. for the unique tracer approach, the CMB without CH_3Cl and the CMB with CH_3Cl included in the model. The composite woodburning fingerprint used is shown in Table 4.D.2. The agreement is good with no significant difference between the unique tracer approach and the CMB without CH_3Cl (paired t-test, $\alpha = 0.01$). The poorest agreements were found on 2/6 and 2/7/84, which were the last two days of a period of extended meteorological air stagnation, when the CH_3Cl concentrations were about 30-40% higher than normal. Referring to Figure 4.C.7 the stagnation period can be seen in the reduced ratios of the concentrations of the reactive species to the less reactive CH_3Cl. It is possible that during this period the CH_3Cl tends to overpredict the aerosol from woodburning because the air stagnation has allowed the longer lived gaseous compounds to build up in in the air over several days while the more reactive species and some of the aerosol may have been removed from the atmosphere.

If the residence time of fine aerosol particles in the troposphere is about 2 to 8 days (Junge, 1963), dependent on the frequency of precipitation, periods of stagnation on the order of one week might result in differential depletion of the aerosols over the gases which continue to accumulate in the ambient air. The effect of this process will be the gradual increase in the background trace gas concentration at the receptor site. A method to correct for this buildup of CH_3Cl from the diurnal woodburning source after a long stagnation period is to examine the frequency response of the receptor area by considering a fixed lid box model with constant wind speed and sinusoidal forcing as suggested by Tennekes (1976). The equation is:

$$H\,[dc/dt + (U/D)c] = q_1 + q_2\sin(wt) \qquad (4.D.1)$$

where H is the height of the mixing layer, c is the concentration of the gas, t is time, U is the wind speed, D is the dimension of the box, q_1 and $q_2\sin wt$ are the source emission terms and w is $2\pi/T$ where T is the period of the sinusoidal forcing which is 24 hours for a diurnal source. The amplitude attenuation A, of the concentration c, derived from the solution to equation 4.D.1 is given by:

$$A = [1 + (wD/U)^2]^{-\frac{1}{2}} \qquad (4.D.2)$$

The amplitude attenuation for a community the size of Hillsboro with a windspeed of 1 mile/hr. is a factor of 0.79. The corrected excess CH_3Cl due to recent emissions is therefore a factor of about 0.79 times the measured excess. Applying this correction factor to the data of February 6 and 7 after several days of air stagnation, the corrected woodburning contributions as estimated using CH_3Cl as a tracer fall within the uncertainty limits of the measured mass and represent more realistic values for the woodsmoke contribution. It is of interest to note that very low ambient elemental to organic carbon ratios occurred on February 3 and 6. Future research should include some examination of potential removal mechanisms for woodsmoke constituents during long periods of air stagnation.

The unique tracer receptor approach predictions of woodsmoke aerosol may be compared with estimates of aerosol from woodburning made from dispersion modeling. Poorer agreement is expected from this comparison than for those made with other receptor model approaches for several reasons. Even under well defined meteorological conditions dispersion models rarely agree on the average with measured pollutant concentrations to better than a factor of 2. When the source of interest is an area source such as woodburning, the large variability of emissions and the common low wind conditions which occur in the evenings allow only a qualitative estimate of pollutant concentrations to be made with a dispersion model. A simple box model was applied on 12 days during the winter of 1984 in Hillsboro and the results of the calculated concentrations of CH_3Cl from woodburning were compared with the measured excess CH_3Cl at the receptor. The steady state box model concentration is calculated as:

$$C_c = (Q_s\ D)/(uH) \qquad (4.D.3)$$

where u is the average windspeed over the sample period measured hourly at the Hillsboro airport, D is the distance from the upwind edge of the area source to the receptor site equal to 3.75 km, Q_s is the source emission factor for CH_3Cl, and H is the mixing height estimated from the 4 AM sounding in Salem, Oregon. The emission rate for CH_3Cl is calculated assuming 34 gm/hr particulate emissions from woodburning (DEQ Woodburning Emission Study, 1984) and applying the relative emission factor for CH_3Cl to particles determined in 4.A. to estimate 0.11 gm/hr per woodstove emission of CH_3Cl. The emission rate is multiplied by the number of households expected to burn wood each evening as evaluated from the DEQ report and divided by the area of emission. The resulting value for Q is 5.3×10^{-9} gm/(m^2sec). For 3 of the days on which very low winds, less than 0.5 m/sec, were recorded or steep temperature inversions were observed from the soundings, the values calulated from the box model are isolated to demonstrate the inability of this type of model to accurately estimate pollutant concentrations under these conditions. Even when the large ventilation time (D/u) of the receptor area is taken into consideration the calculated concentrations are still more than a factor of two above the measured ones. The concentrations of CH_3Cl estimated on the other days agreed with the measured values to within 50% on the average. The results of the comparison are presented in Table 4.D.3.

All source apportionment approaches examined tend to support the accuracy of the unique tracer approach for estimating ambient woodsmoke concentrations using the gas CH_3Cl. In particular the results of the multicomponent chemical mass balance comparisons are encouraging since this model relies on a combination of other species associated with woodburning unrelated to CH_3Cl. The chemical mass balance approach applied to residential woodburning weights most heavily the organic carbon concentrations and since the variability of organic carbon in the woodburning source emisions is comparable to that of CH_3Cl both approaches probably estimate the residential woodburning source to the same degree of accuracy in a community like Hillsboro with few other sources of organic carbon. However where there are other major sources of organic carbon, such as heavy automobile traffic or industrial sources, or where there are collinear sources as discussed in Chapter 2.D, the unique CH_3Cl approach to assessing the woodburning contribution may be preferable. In the next chapter the implications of the estimated concentrations of woodsmoke in the ambient air calculated with the CH_3Cl tracer approach are examined.

Table 4.D.1

Comparison of the Multicomponent CMB Apportionment of S_j in μg/m^3 of the Woodburning Component of the Aerosol with that of the CH_3Cl Unique Tracer Approach Using the CMB Model (NEA, 1984) and the woodstove source profile developed in this work.

Sample Period (start date)	S_j CH_3Cl Unique	S_j CMB without CH_3Cl	S_j CMB with CH_3Cl	Total Measured Mass
1/17/84 6pm-6am	53 ± 13	59 ± 8	58 ± 8	66 ± 3
1/19/84 6pm-6am	40 ± 13	48 ± 7	45 ± 6	55 ± 3
1/26/84 6pm-6am	41 ± 13	49 ± 8	46 ± 6	48 ± 2
1/27/84 6pm-6am	33 ± 13	37 ± 6	36 ± 5	32 ± 2
2/2/84 6-9pm	94 ± 17	108 ± 20	103 ± 15	106 ± 11
2/3/84 6-9pm	58 ± 13	51 ± 5	46 ± 7	51 ± 5
2/3/84 9pm-6am	37 ± 12	55 ± 9	41 ± 5	53 ± 3
2/6/84 6pm-12am	94 ± 17 74 ± 13*	71 ± 12	74 ± 8 72 ± 10*	82 ± 6
2/7/84 6pm-12am	53 ± 13 42 ± 13*	43 ± 7	45 ± 4 43 ± 6*	37 ± 3

*The CH_3Cl background values were corrected on these days; see text for explanation. The unstarred values are the calculations for the uncorrected background values.

Table 4.D.2

Woodburning Source Composition Developed in This Work and Used in the CMB Calculations

Species	Percent Fine Particulate Mass
Na	0.083 ± 0.012
Mg	0.073 ± 0.017
Al	0.038 ± 0.122
Si	0.051 ± 0.204
Cl	0.228 ± 0.674
K	0.472 ± 1.412
Ca	0.046 ± 0.113
Ti	0.002 ± 0.005
V	0.002 ± 0.004
Cr	0.002 ± 0.005
Mn	0.002 ± 0.005
Fe	0.003 ± 0.007
Ni	0.002 ± 0.005
Zn	0.037 ± 0.094
Br	0.005 ± 0.011
Pb	0.010 ± 0.021
CH_3Cl	0.310 ± 0.030
OC	49.780 ± 5.584
EC	8.700 6.163
Sum	59.846

TABLE 4.D.3

Steady State Box Model Calculations of Methyl Chloride Concentrations, C_c, in Hillsboro Compared with Measured Concentrations, C_m.

Date	Calculated C_c pptv	Measured C_m pptv	$\frac{C_c - C_m}{C_m}$
1/10/84	182	152	+ 0.20
1/13/84	32	144	- 0.78
1/19/84	210	80	+ 1.63
1/22/84	64	112	- 0.43
2/25/84	130	89	+ 0.46
2/27/84	61	17	+ 2.59
2/28/84	30	52	- 0.42
3/1/84	35	18	+ 0.94
3/21/84	53	42	+ 0.26
		Average ± Standard Error	+0.49 ± 0.36
DAYS WITH LOW WIND SPEED OR STEEP INVERSION LAYER			
1/7/84	1116	139	+ 7.03
1/16/84	1090	211	+ 4.17
2/26/84	455	102	+ 3.46
		Average ± Standard Error	+ 4.89 ± 1.09

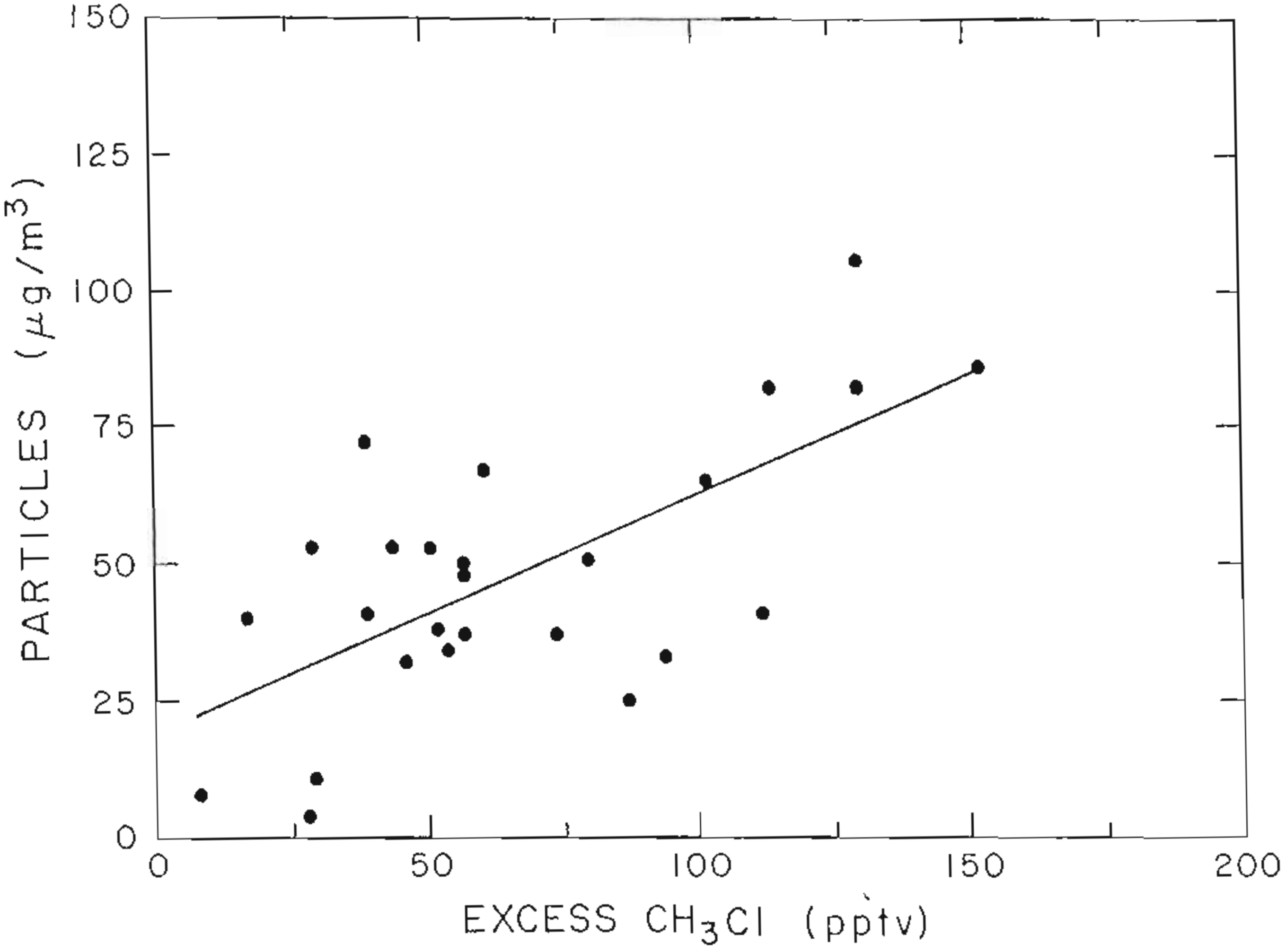


FIGURE 4.D.1: Excess CH_3Cl Concentration from Integrated Samples versus Fine Particle Concentration in Hillsboro, Oregon in the Evening during the Winter

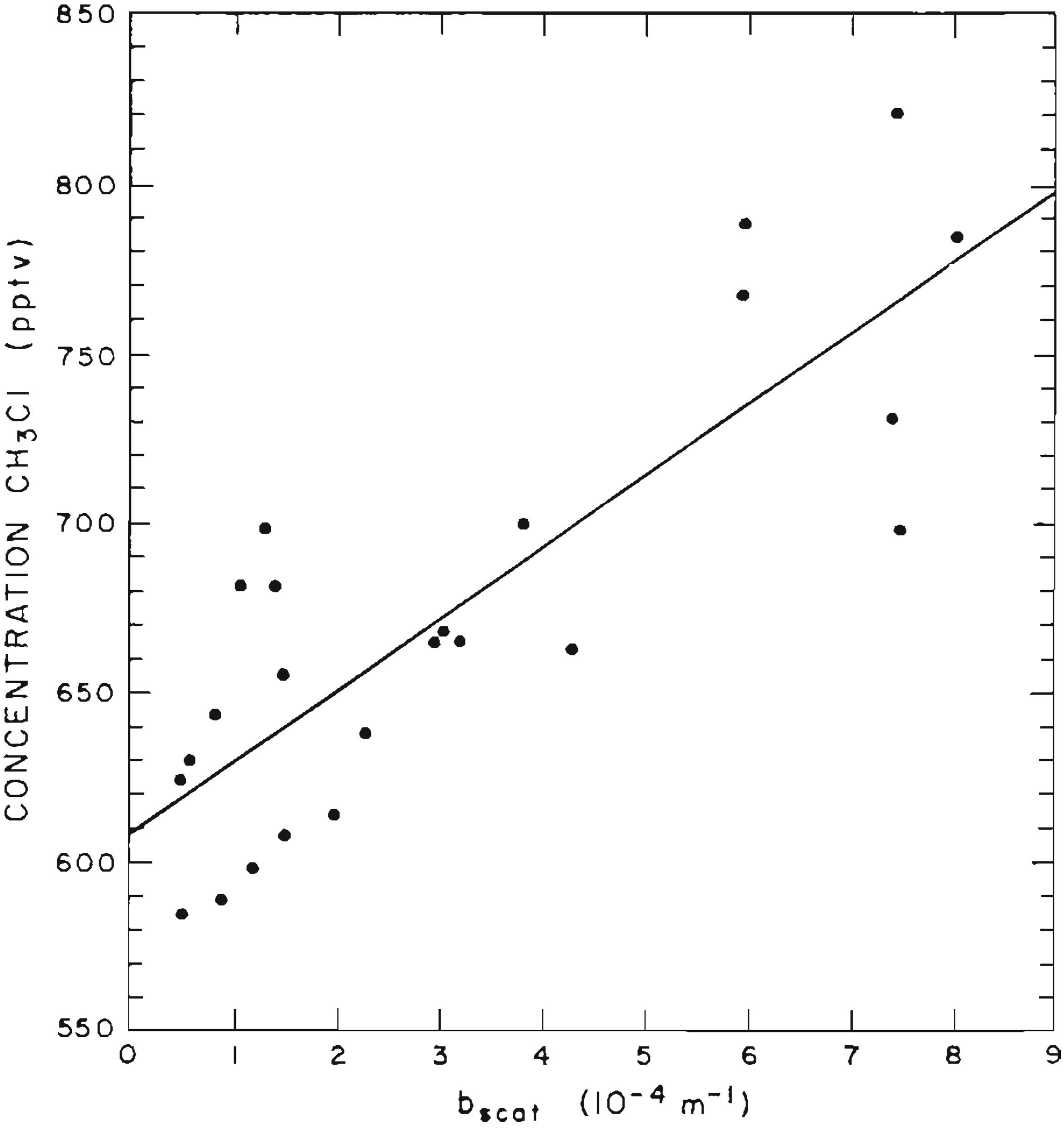


FIGURE 4.D.2: CH_3Cl Concentrations from Grab Samples versus Light Scattering Coefficient, b_{scat}, on Winter Evenings in Hillsboro, Oregon (Khalil et al., 1983a)

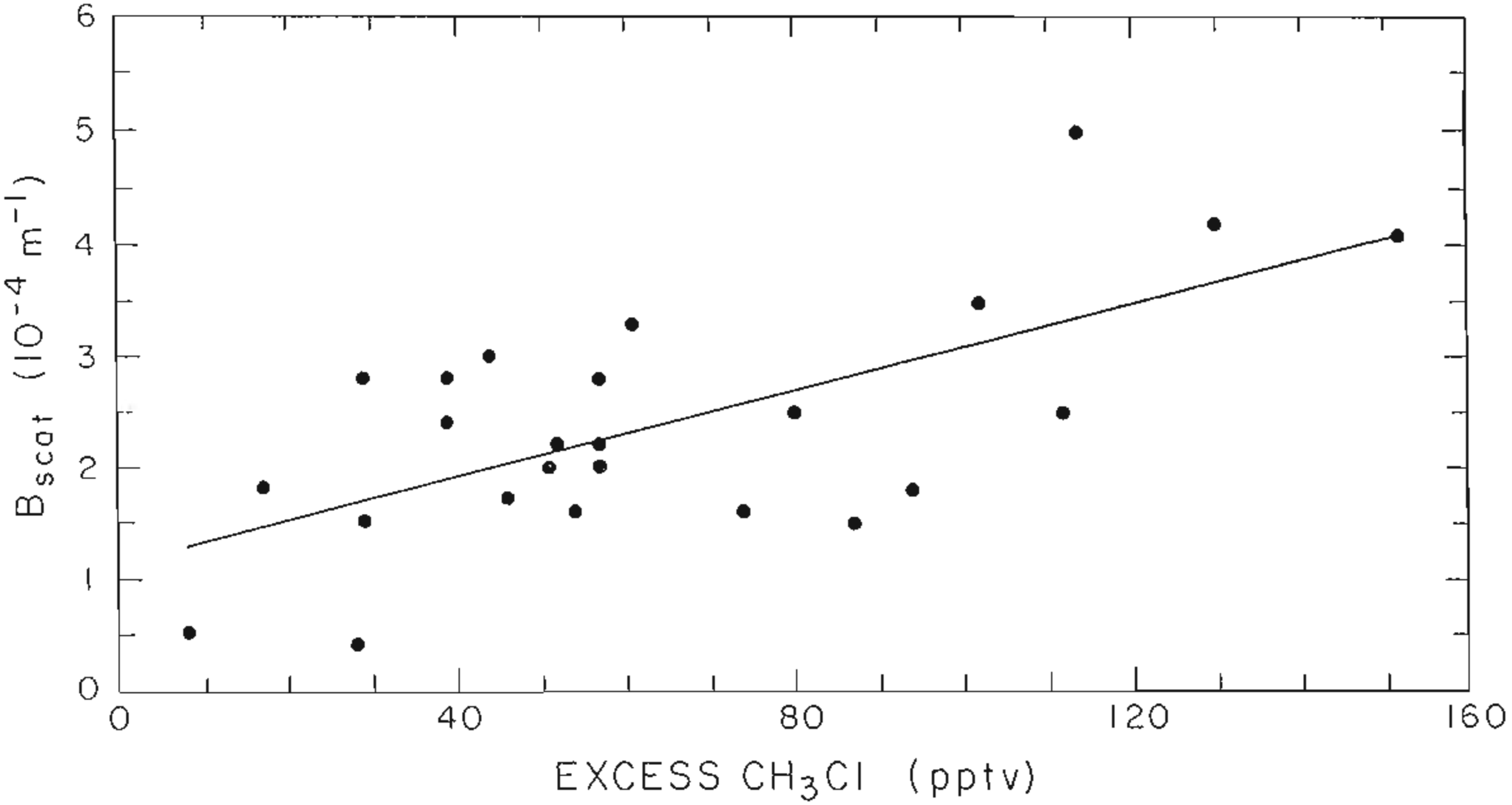


FIGURE 4.D.3: Excess CH_3Cl Concentration from Integrated Samples versus Light Scattering Coefficient, b_{scat}, in Hillsboro, Oregon

CHAPTER 5

IMPLICATIONS: Estimates of Exposure to Fine Particles from Woodburning Using the CH_3Cl Tracer Approach

5.A. Model of Personal Exposure to Woodburning Pollutants

An advantage in the use of gaseous species to trace air pollution sources is the almost real time measurements which can be made, from continuous monitoring methods to those on the order of several minutes in the case of grab samples. The measurements of the gaseous concentrations, including those of methyl chloride, which are presented in this work are made over periods as short as 2-5 minutes. The frequency of collecting ambient samples to be analyzed for methyl chloride is limited only by the economics of analyzing a large number of samples in the laboratory, the current time per analysis being about 10 minutes per sample. Sampling periods for collection of particulate material are generally several hours, dependent upon the total fine particulte mass concentrations, to meet the requirements of the analytical techniques for accurate analysis of elemental species. Short period pollutant concentration information is useful in estimating human exposures to high concentrations which occur over short intervals of time and which might constitute acute exposure. Some evidence for acute exposure to woodsmoke has been suggested (Edgerton et al., 1985, Appendix B).

In order to assess whether a certain pollutant or class of pollutants represents a health hazard to the public, the extent of exposure to the pollutant must be ascertained. Personal exposure information may be obtained by the use of personal monitoring equipment which is worn on the individual or by estimation of exposure through theoretical models using concentration information from fixed monitoring sites in many different environments and activity profiles of the individual. While there has been considerable development of personal monitoring equipment recently (Mintz et al., 1982; Wallace et al.,1982; Fletcher et al., 1984), there have been few large scale studies and most monitors are pollutant-specific, making it difficult to characterize the effects of combined pollutant exposures. In general, indirect methods of exposure estimation may be less expensive. Though indirect methods may be subject to large prediction errors due to the inability of fixed monitoring sites to represent concentrations over larger regions, direct personal exposures when extrapolated to the population as a whole also have large prediction errors.

The exposure of an individual to a pollutant is a measure of pollutant concentration available to the body while the dose is the actual quantity which enters the body. Exposure calculations are used to estimate dosages. The total exposure is the product of the concentration of pollutant times the length of exposure. Since the length of exposure in an environment may vary from a few minutes to many hours, the concentration information must be representative of the concentration over the particular period of individual exposure. Concentrations of fine particulate matter measured on filter samples is generally given over a 24 hour averaged period and this may underestimate a short term exposure by a factor of 2 or 3 (Edgerton et. al., 1984b). As the sample collection averaging time becomes shorter, the probability of detecting very high concentrations increases. These short periods of high concentrations may play an important role in causing acute health effects. Because collection and analysis of filter media generally requires large samples, the use of surrogate gaseous tracers may be the only means of evaluating the very short term high concentrations of particulate pollution to which individuals might be exposed.

Acute Exposure to Woodsmoke

Acute exposure to woodsmoke might engender effects ranging from irritation of the mucous membranes to exacerbation of chronic respiratory disease. It has been shown that exposure to fumes from the pyrolysis of abietic acid can cause moderate to severe irritation of the eyes, nose and throat (Documentation of the TLV for Substances in Workroom Air, 1971) and can cause attacks of asthma (Fawcett et al., 1976). It is also known that abietic acid is found in wood dust and in smoke from wood combustion (Sigman et al., 1984 and Prakash et al., 1972). An acute exposure level of 40 $\mu g/m^3$ is a rough estimate based on the recommended threshold level value (TLV) of the exposure of seasoned industrial workers to the concentration of fumes from the pyrolysis of gum rosin (abietic acid) as measured indirectly as the concentration of aliphatic aldehydes (Documentation of the TLV for Substances in Workroom Air, 1971), using a safety factor of 1/10 for extrapolation to the general population and estimates of the ratio of aldehyde to particle emission from the burning of wood in stoves (DeAngelis et al., 1981).

Using the rough definition of acute exposure to woodsmoke developed in the previous paragraph and referring back to Figure 4.C.5 it is evident that the potential for acute exposure in Hillsboro is very large. Woodsmoke contributions, as estimated using the CH_3Cl tracer approach, exceeded 40 $\mu g/m^3$ for over 50% of the evening and 40% of the morning samples. Though the Portland samples were very short period, on the order of only a few minutes, high contributions from woodsmoke may result in the frequent acute exposures in the Portland Lafayette neighborhood. The effects of woodsmoke at contributions just above the 40 $\mu g/m^3$ acute level are likely to affect mainly those members of the population susceptible to respiratory illnesses. While there is currently no direct evidence linking asthma to woodsmoke, an increase in respiratory complaints has been shown to occur on evenings when it is evident that there is a high concentration of woodsmoke in the air (Lawyer,1984).

Chronic Exposure to Woodsmoke

It is difficult to assess chronic effects from a specific air pollution event due to the long latency period between the exposure and the health effect, during which the individual has been exposed to many other chemical and environmental agents which could also play a role in causing adverse health conditions. However, the integrated exposure to various pollutants over some time period, for example one week, may be compared and some conclusions may be drawn as to the relative risk of different types of pollution. A daily integrated exposure to woodsmoke will be estimated in this section for a "typical working individual" and for a "typical homemaker" or unemployed person who spends most of his or her time indoors and compared to the standards set for industrial and ambient exposures.

Corn (1971) characterized worst case dosages to the respiratory system based on pollutant standards for two categories of exposure, community and occupational, and compared these exposures to potential personal exposures such as that from cigarette smoke. Fugas (1975) made one of the first attempts to estimate pollutant exposure from fixed site concentration data. She calculated a weighted weekly exposure to sulfur dioxide, lead and manganese based on ambient concentrations and the concentration in the home given the number of hours per week spent in each of these environments. Ott (1980) and Moschandreas (1979 and 1981) also applied similar models to estimate personal exposure to air pollution. The estimates of woodsmoke concentration from the previous chapter will be used to calcuate daily dosages of woodsmoke assuming the outdoor exposure to be the average wintertime integrated concentration measured during each of the four time periods sampled over the day in the wintertime in Hillsboro and shown in Table 5.A.1

Indoor concentrations of woodsmoke in homes where there is wood being burned have been estimated by Moschandreas (1980) and Core (1981). The concentrations vary widely with the individual home and certainly fluctuate greatly over the day, the highest concentrations occurring during the stoking of the fire as indicated by the spikes of CO concentrations observed by Moschandreas. An average concentration of 20 $\mu g/m^3$ falls within the limits found for estimates of indoor concentrations of excess fine particles during woodburning and will be used for this calculation for the indoor concentration of woodsmoke in homes burning wood. The indoor concentration of fine particles from woodsmoke will be assumed to be zero in homes where there is no operating wood burning devices.

It is assumed that the employed person spends one hour in the morning and evening period outdoor in transit to and from work and 1 hour during the lunch period in the outdoor environment. The unemployed person is assumed to spend 2 hours in the afternoon in transit and in outdoor activities. The concentration of woodsmoke to which a person in each category is exposed during each period for woodburning household, WB, and for non-woodburning household, NWB, is shown in Table 5.A.1 and Table 5.A.2. For the employed person the average daily exposure to woodsmoke is 13 $\mu g/m^3$ for the individual in the woodburing home and 4 $\mu g/m^3$ for the individual in the non-woodburning home. The corresponding concentration for the unemployed person is 18 $\mu g/m^3$ in the woodburning home and 1 $\mu g/m^3$ in the non-woodburning home. It is obvious that the indoor exposures dominate the total dosage of woodsmoke that an individual receives over the day.

A total daily intake of 0.2 mg of fine particulate material from woodsmoke is calculated for the maximum personal exposure assuming 10 m^3/day air intake per individual, Corn (1981). More recent estimates of air intake suggest almost a doubling of the this figure (International Commission of Radiological Protection, 1974). This exposure is compared with the worst-case exposure to particulate matter and to carbon monoxide as estimated by Corn (1971), based on ambient and occupational standards in Table 5.2. The comparison suggests that the typical long-term dosage of woodsmoke to a healthy individual is not significant relative to other types of exposure the individual might encounter. If polycyclic organic material (POM) is assumed to make up on the order of 1% of the fine particulate material of woodsmoke (Rudling et al., 1982; Hubble et al., 1982; Peters et al., 1982; Ramdahl et al., 1982), the maximum daily intake of POMs from woodburning is around 2 μg/day which is much less than the 10 μg/day estimated threshold limit value for POMs derived by DeAngelis et al. (1981) from data of Handy et al. (1976). However, the maximum daily intake of benzo(a)pyrene (BaP) from wood combustion may be estimated to be around 0.2 μg/day assuming the BaP/fine particle ratio in woodsmoke to be about 0.1% (Rudling et al., 1982; Ramdahl et al., 1982). This intake is 4 times the estimated allowable daily intake of BaP (Howard et al., 1982) although it is less than the intake of a cigarette smoker or the intake from food consumption (Howard et al., 1982). If the BaP intake can be considered to be representative of the intake of carcinogenic material from woodsmoke, then there may be considerable risk to susceptible persons of long term adverse health effects such as lung cancer from burning wood in the home. The daily intake of non-woodburners who are employed or unemployed is below the estimated daily allowable intake.

The most important health risk from woodsmoke pollution may be the risk of acute exposure to susceptible members of the population, whose clean air requirements may not necessarily be met by the current air quality standards. The use of surrogate tracers for woodsmoke, such as CH_3Cl, which may be measured over very short time periods, may be a first step toward the evaluation of very high exposures to woodsmoke over brief periods of time. Immediate asthmatic reactions to fumes from "multicore" solder, the principal constituent of which is abietic acid which is also found in woodsmoke, has been shown to occur in some subjects with only 3-10 breaths (Fawcett et al., 1976). The future direction of study in assessing health risks from residential wood combustion needs to address the pollutant exposure of those members of the population who are susceptible to acute reactions to specific respiratory irritants. In the next section the societal implications of health risks from woodburning pollution will be discussed.

TABLE 5.A.1

Daily Integrated Exposure to Woodsmoke for Persons Employed Indoors In Office Buildings

Microenvironment (ME) (# hours spent in ME in period 1,2,3,4)		Concentration of Fine Particles from Woodburning μg/m^3							
		Period 1 6-10am		Period 2 10am-6pm		Period 3 6pm-2am		Period 4 2-6am	
		WB*	NWB	WB	NWB	WB	NWB	WB	NWB
Home	(2,0,7,4)	20	0	20	0	20	0	10	0
Work	(1,7,0,0)	0	0	0	0	0	0	0	0
Street	(1,1,1,0)	29	29	19	19	42	42	24	24
Average for Period		17	7	2	2	23	5	10	0

Total Daily Average: WB Household 13 μg/m^3

NWB Household 4 μg/m^3

*WB means woodburning household and NWB means nonwoodburning household

TABLE 5.A.2

Daily Integrated Exposure to Woodsmoke for Persons Who Spend Most Of the Day In the House

Microenvironment (ME) (# hours spent in ME in period 1,2,3,4)		Concentration of Fine Particles from Woodburning µg/m³							
		Period 1 6-10am		Period 2 10am-6pm		Period 3 6pm 2am		Period 4 2-6am	
		WB*	NWB	WB	NWB	WB	NWB	WB	NWB
Home	(4,6,8,4)	20	0	20	0	20	0	10	0
Street	(0,2,0,0)	29	29	19	19	42	42	24	24
Average for Period		20	0	20	2	20	0	10	0

Total Daily Average: WB Household 18 µg/m³

NWB Household 1 µg/m³

*WB means woodburning household and NWB means non-woodburning household

TABLE 5.A.3

Comparison of Potential Occupational and Ambient Dose per Day to the Respiratory Tract for Particulate Matter and CO *

	Occupational 8 hrs at TLV	Ambient 24 hrs at standard	Cigarette Smoke 20/day	Ambient Woodsmoke 24 hrs	Indoor Woodsmoke 24 hrs
Particulate Matter	80 mg (nuisance dust) 0.8 mg (lead dust) 8.0 mg (cotton dust) 24 mg (coal dust)	0.65 - 1.0 mg	120-520 mg	0.29 mg	0.18 mg
Carbon Monoxide	400 ppm-hrs	480 ppm-hrs	45,000-85,000 ppm hrs	24 ppm-hrs	70 ppm-hrs

*Occupational, Ambient and cigarette smoke from Corn, 1971; indoor woodsmoke estimated using data from Moschandreas, 1980; ambient woodsmoke from this work.

5.B Societal Implications of Residential Wood Combustion as a Major Contributor to Air Pollution

While the growing use of wood as a secondary home heating fuel in the United States is a cause for concern over increased health risks, the use of wood fires in many developing countries is the dominant energy source for heating and cooking. It is estimated that about half of the world's households cook with biomass fuels: wood, crop residues and animal dung (Smith et al., 1984), in indoor environments with little ventilation; and that 300-400 million people worldwide may be affected by health problems associated with biomass burning (DeKoning et al., 1985). Concentrations of CH_3Cl above those found in the U.S. have been measured in urban and rural China (Rasmussen et al., 1982) indicating a dense population of smoldering fires. The average CH_3Cl concentration of 5 samples collected outdoors in a small village in Nepal was 0.8 ± 0.5 ppb compared to 7.6 ± 3.7 ppb for 4 samples collected inside homes in Nepal and analyzed at the Oregon Graduate Center. This corresponds to fine particulate levels inside homes of about 4 mg/m^3 which is consistent with the 4-6 mg/m^3 measured by Smith et al., 1984 in a simulated village kitchen. Exposures to pollutants from woodsmoke in developing countries to those who spend most of their time inside, mostly women and children, is several orders of magnitude over exposures experienced in the industrialized world.

The practice of cooking on open fires is an integral aspect of the cultural life in many countries, but it is an inefficient means of using the heat generated from firewood and the lack of a flue to direct the exhaust products of the fire away from the living area increases the levels of exposures to woodsmoke pollutants. The introduction of efficient woodburning stoves in these areas would not only reduce pollutant exposures, but would mitigate the fuelwood shortages which are reaching crisis proportions in many developing areas. A suggestion for alleviating fuelwood shortages has been the encouragement of agro-forestry, or incentives to local farmers to grow their own firewood on community woodlots using fast growing "energy" trees. In any event it seems likely that continual use of biomass fuels as a major energy source is likely to occur in much of the world.

Emissions from biomass combustion are an important global source of gases which may potentially alter the earth's climate, such as those associated with the greenhouse effect, CO_2, CH_4, and N_2O, which is postulated to cause an increase in the earth's temperature. It is also a source of gases important in stratospheric chemistry, such as CH_3Cl which may play a major role in regulating the concentrations of ozone shielding the earth from ultraviolet radiation, and carbonyl sulfide (COS) which contributes sulfur to the stratospheric sulfate layer. The particulate emissions from biomass burning may contribute significantly to the global burden of tropospheric aerosols, especially organic and elemental carbon. Increases in the concentration of tropospheric aerosols can cause either a cooling or heating effect dependent on the radiative properties of the aerosol. Because elemental carbon aerosol are light absorbers, the effect of increased elemental carbon may be a warming of the earth. The burning of wood globally as a fuel and for commercial purposes makes up an average of only 15% of the biomass burned annually (Crutzen et al., 1979). The largest biomass burn activity is related to agricultural practices, such as the burning of agricultural wastes and the burning of material from land cleared for farming. The agriculturally related contribution to the annual quantity of biomass burned is on the average 53% (Crutzen et al., 1979).

Because the amount of forested land is decreasing, there is a natural limit to the biomass reserve which can be burned for the purposes of shifting agriculture, and that which is readily available for use as fuel or for commercial purposes in developing countries. However, with the emphasis on utilization of bio-wastes for producing energy, it is possible that in the future the major activity contributing to biomass burn emissions will be shifted from agriculture practices to the practice of using biomass for the commercial production of energy. While the continued use of fossil fuels may lead to a faster buildup of gases associated with the greenhouse effect and other climate altering processes, a switch to biofuels may present a new set of environmental concerns such as increased emissions of polycylic organic material. The centralization of energy production may facilitate emission control, but the existence of many small regional producers is probably a more sociologically acceptable solution in developing areas of the world. In any event, a balance must be drawn between a culturally and economically acceptable source of energy and the individual and community health of the people.

To summarize, the major concern over the increased use of wood as a residential fuel is the increased exposure to potentially harmful compounds emitted within the home and into the ambient air. The populations which experience the greatest risk are those with sensitivities to woodsmoke, those with chronic respiratory disease and pariticularly those who live in parts of the world where the burning practices take place in homes with little ventilation and the exposures are orders of magnitude above levels that would be considered acceptable in the United States. The concern over increased biomass emission as a potential climate altering activity deserves future study. The tremendous variability found in the particulate and gaseous emissions in woodburning stoves in this dissertation point out the caution that should be used in extrapolating local emission rates to global ones. Possible future directions for expansion of this research to better assess both the local and global concerns of woodburning emissions are addressed in the Summary.

SUMMARY

In this research, a gaseous species has been used as a surrogate tracer to characterize the contribution of a source to fine particulate air pollution. It has been demonstrated that methyl chloride (CH_3Cl), an inert gas, is unique to biomass burning in residential neighborhoods and can be used to assess the contribution of residential woodburning emissions to ambient fine pariculate pollution. The concentration of fine particulate material from residential woodburning in Portland, Oregon has been estimated over time periods as small as several minutes to be as high as 300 $\mu g/m^3$ and the daily contribution has been estimated in periods of 3 to 4 hours to average about 40 $\mu g/m^3$ in the evenings. These results represent an improvement in the time resolution of source apportionment methods from particulate samples which usually estimate source contributions over 12 to 24 hours. This increased time resolution in concentrations of woodsmoke has enabled better estimates of personal exposure to woodsmoke related pollutants. The

concentrations of woodsmoke estimated using the CH_3Cl tracer model have been validated by demonstrating the consistency of the results of the CH_3Cl model with those of other techniques applied concurrently. The addition of CH_3Cl to the source characterization of residential wood combustion in an area where several sources have similar source compositions can greatly reduce the uncertainties in the source apportionments.

The contributions of this work include (1) the development and testing of ambient and source characterization methods for CH_3Cl and other gases as applied to receptor models, (2) the incorporation of gaseous as well as particulate phase species into the mass balance receptor model, and verification that the CH_3Cl used in a tracer solution provides equivalent results, (3) the application of an analytical method to determine the potential interference between similar source compositions and (4) the characterization of various gaseous species in woodsmoke emissions.

The use of CH_3Cl specifically as a tracer is limited by its large background concentration which reduces the confidence limits with which the woodburning source can be apportioned. A major limitation in the use of gaseous species to apportion sources of particulate material is the potential for the differential removal of the two phases. This may include gas phase reactions, aerosol scavenging, particle deposition, and other mechanisms of gas or aerosol depletion. Differential removal may especially be a problem when pollutants are transported over great distances or are trapped in the boundary layer over several days. However if the relative depletion processes of the gas and the aerosol can be well characterized, the differential depletion itself may be used to identify the sources involved in long distance transport. The relative depletion ratio of the gas/aerosol may be used to determine the age of the sampled air mass and with wind trajectory analysis may be used to determine its source area. Under conditions of air stagnation in urban areas, the differential depletion may be used to differentiate the portion of the pollutants which have been in the air for several days from that which has been recently emitted. This type of information may be particularly important for health assessment of woodsmoke pollutants as it has been shown that mutagenic changes may take place in dilute wood smoke which reacts with O_3 and NO_2 during the day (Kamens et al., 1984, 1985). The characterization of differential depletion of gases and aerosols in tracer studies is an area for future research and has the potential for greatly enhancing the ability of receptor models to characterize air pollution.

Another area for future research in the application of gaseous tracers to atmospheric studies is the extension of receptor models to estimate sources of long distance pollutant transport, such as in artic haze, and to apportion the contribution of various source areas to global trace gas budgets. The application of receptor models in studies of global chemistry may help resolve the contribution of biomass combustion, from that of other sources, to the gases which may potentially alter the earth's climate. This knowledge may have implications on worldwide strategies for energy production. Together the combination of particulate and gaseous characterization of the source types or source areas which contribution to atmospheric emissions may be used to gain a better understanding of both local air pollution and global atmospheric processes.

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VITA

Sylvia Anne Edgerton was born in Charlotte, North Carolina on September 19, 1951. She graduated from the University of Arizona in Tucson, Arizona with a B.S. in Physics and a B.S. in Astronomy in 1977. As an undergraduate, she taught an introductory physics laboratory. She also worked for two years at the Lunar and Planetary Laboratory in Tucson doing scientific data reduction in the study of planetary atmospheres.

In 1978, she was employed by the Pima County Air Quality Control District in Tucson as an Air Quality Instrumentation Technician. In 1979, she was promoted to Air Quality Analyst. In 1980, she came to the Oregon Graduate Center to enter the doctoral program in Environmental Science.

Sylvia was married to Darrell William Joseph in 1984. She has one daughter, Erin McKenzie Edgerton, age 6.