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University of Alberta

Methoxylated Phenols as Tracers for Wood Smoke Carbonaceous Inhalable Particulate Matter (PM_{10})

By

Anthony Kwong-hung Mak 

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science

in

Medical Sciences – Public Health Sciences

Edmonton, Alberta

Spring, 1999

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Methoxylated Phenols as Tracers for Wood Smoke Carbonaceous Inhalable Particulate Matter (PM_{10}) submitted by Anthony Kwong-hung Mak in partial fulfilment of the requirements for the degree of Master in Science, Medical Sciences - Public Health Sciences.

Steve E. Hrudey
Supervisor

Kenneth Froese
Co-supervisor

Warren Kindzierski
Committee Member

X. Chris Le
Committee Member

15 April 1999

Date of Approval

To Winnie,

for standing by me as always;

to my children Stephanie and Justin,

for their sacrifice and understanding;

and

to my Lord,

for giving me wisdom.

ABSTRACT

Four types of firewood, that are indigenous to the Alberta region, birch, poplar, pine and spruce were burned outdoors under "hot-burning" conditions in a domestic wood-burning stove. Results confirmed that the total quantity of guaiacol, 4-methylguaiacol and 4-ethylguaiacol is highly correlated with the overall quantity of all guaiacol species. Vanillin can be a significant combustion by-product, for certain wood types, under certain combustion and environmental conditions. Accordingly, vanillin should be treated as a major combustion by-product. Under controlled combustion conditions, various wood types produced similar smoke signatures in this study. However, a "universal" wood smoke signature was found to be unrealistic, because the quantity and diversity of combustion by-products are influenced by the wood type and combustion conditions. The source apportionment of wood smoke originated from a point source, an industrial wood residue burner, for example, is feasible using the receptor modelling with a smoke profile determined simultaneously during ambient sampling. However, source apportionment of residential wood combustion with multiple sources, such as wood burning fireplaces and stoves, is likely not feasible with this method due to the difficulty in establishing a representative "average" combustion condition.

ACKNOWLEDGEMENTS

I sincerely thank Dr. Steve Hrudey and Dr. Ken Froese, my program supervisors, for their acceptance, guidance and patience over the years.

Dr. Warren Kindzierski and Dr. Chris Le critically reviewed the original version of this thesis. Their comments not only have greatly improved the quality of this thesis, their input has also exemplified the multi-disciplinary nature of the sciences of environmental health.

Also, I thank Ms. Linda Kimpe and Mr. Jeff Rose, who both often went beyond the call of duties and extended their helping hands during difficult times.

I am grateful to Dr. Sharle Wu and her staff at the Alberta Research Council. They demonstrated professionalism at the highest level during the course of this research project.

Mr. John O'Laney and Mr. Nelson Fok, my mentors at work, guided me through this path. Without their vision, inspiration, support and encouragement, I would have stayed where I was.

Lastly, I must thank Alberta Health for the generous financial support that has made this study possible.

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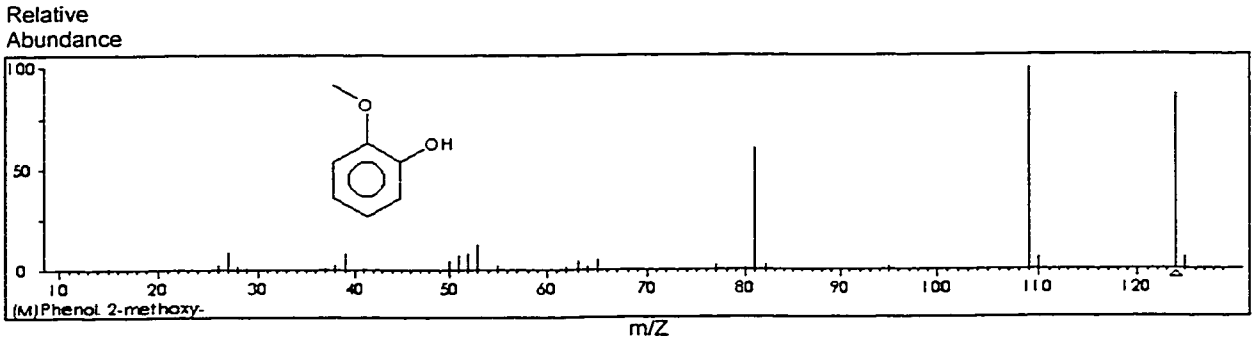
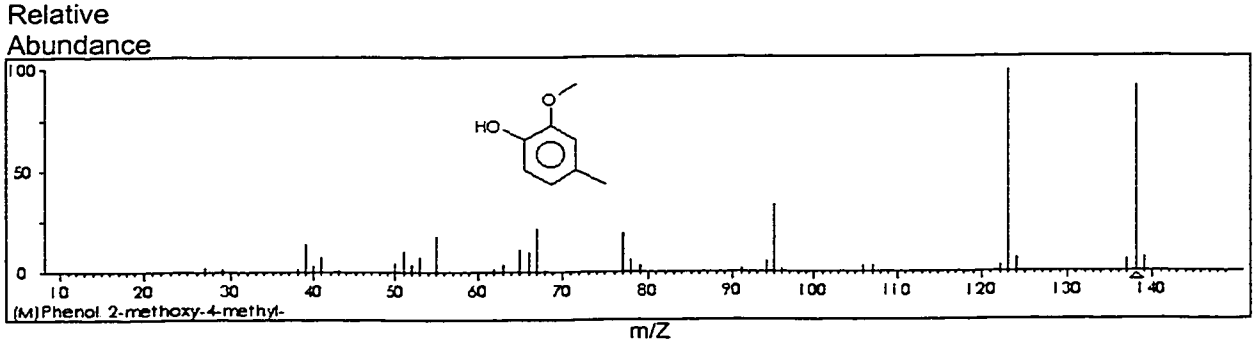
1. GUAIACOL
   Formula: $C_7H_8O_2$
   MW: 124 CAS#: 90-05-1 NIST#: 228856 ID#: 49520
   Synonym:
   1-Hydroxy-2-methoxybenzene

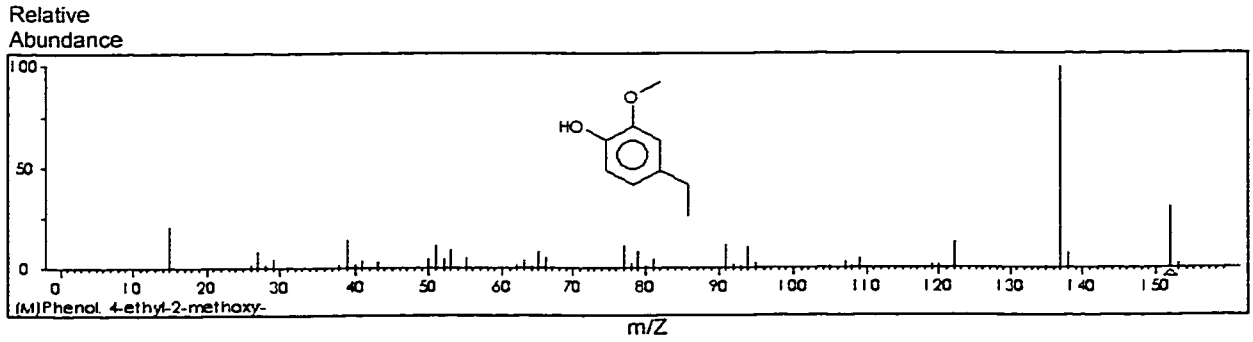


2. 4-METHYLGUAIACOL
   Formula: $C_8H_{10}O_2$
   MW: 138 CAS#: 93-51-6 NIST#: 76340 ID#: 56062
   Synonym:
   2-Methoxy-4-methylphenol

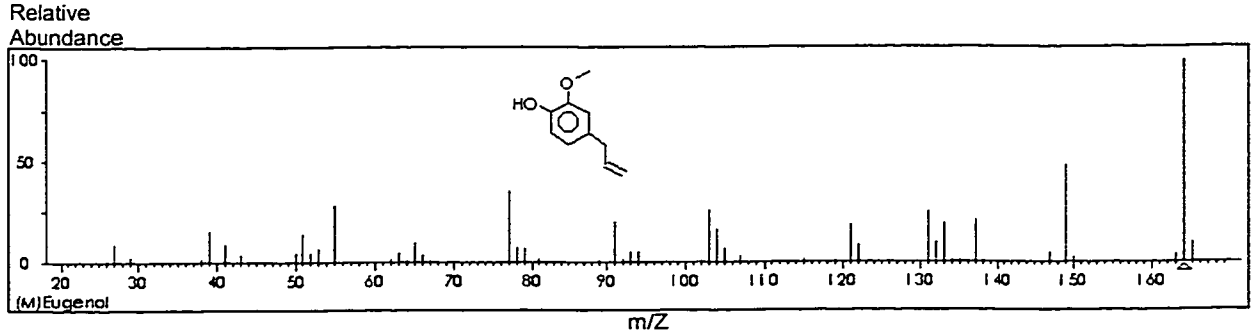


LIST OF COMPOUNDS

3. 4-ETHYLGUAIACOL
   Formula: $C_9H_{12}O_2$
   MW: 152 CAS#: 2785-89-9 NIST#: 135148 ID#: 62446
   Synonyms:
   4-ethyl-2-methoxy-Phenol



4. EUGENOL
   Formula: $C_{10}H_{12}O_2$
   MW: 164 CAS#: 97-53-0 NIST#: 249195 ID#: 72243
   Synonym:
   Phenol, 2-methoxy-4-(2-propenyl)-



LIST OF COMPOUNDS

5. VANILLIN
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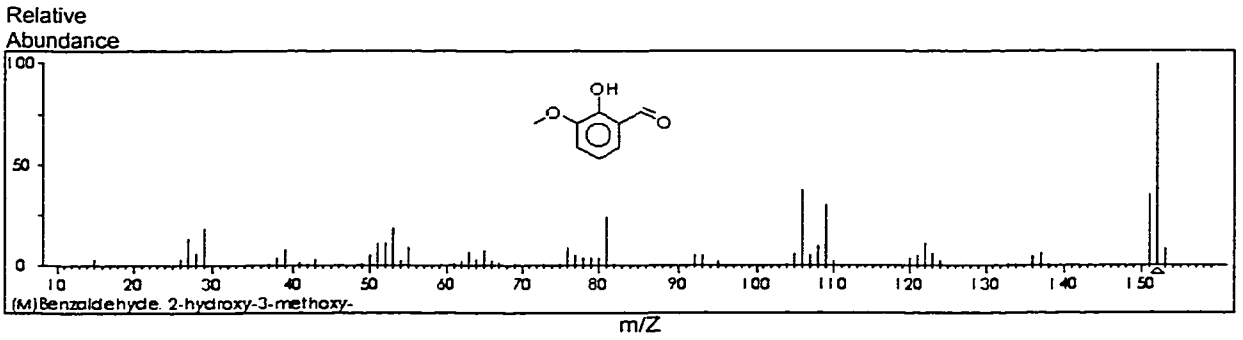
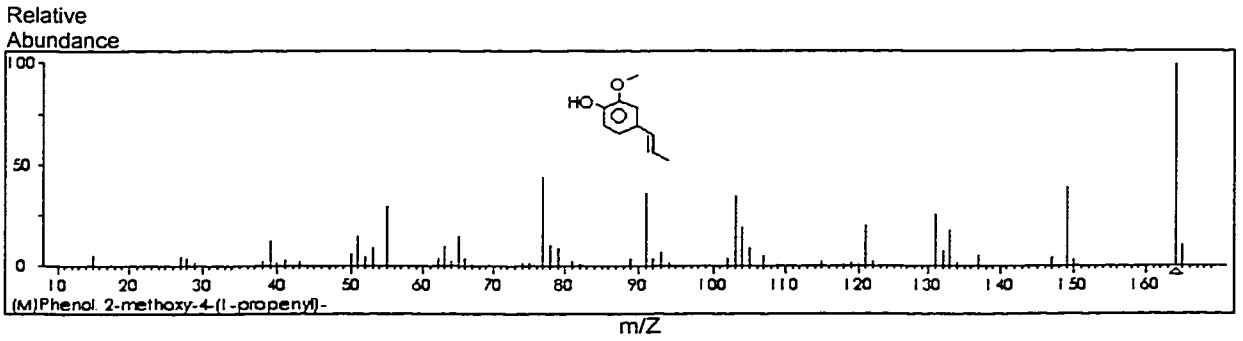
   Synonym:
   2-Hydroxy-3-methoxybenzaldehyde



6. ISOEUGENOL
   Formula: $C_{10}H_{12}O_2$
   MW: 164 CAS#: 97-54-1 NIST#: 113236 ID#: 72096
   Synonym:
   2-Methoxy-4-(1-propenyl)phenol



LIST OF COMPOUNDS

7. ACETOVANILLONE
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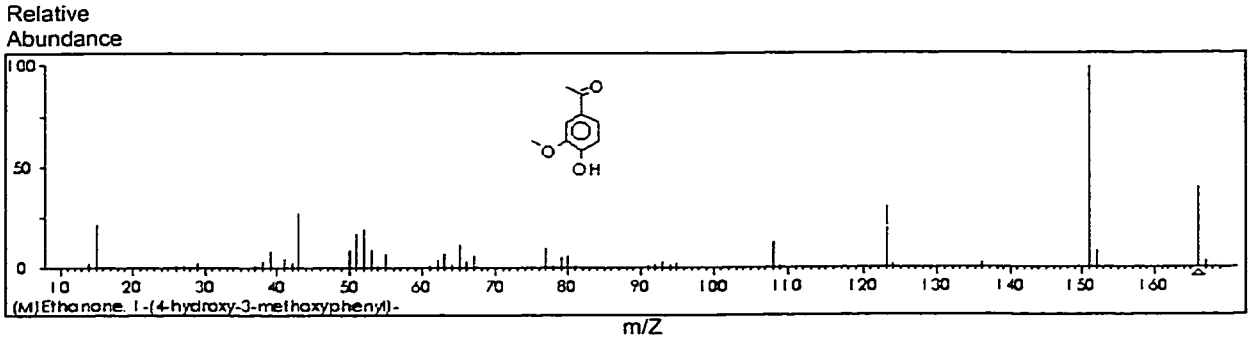
   Synonym:
   Acetophenone, 4'-hydroxy-3'-methoxy-



8. 4-BROMOACETOPHENONE
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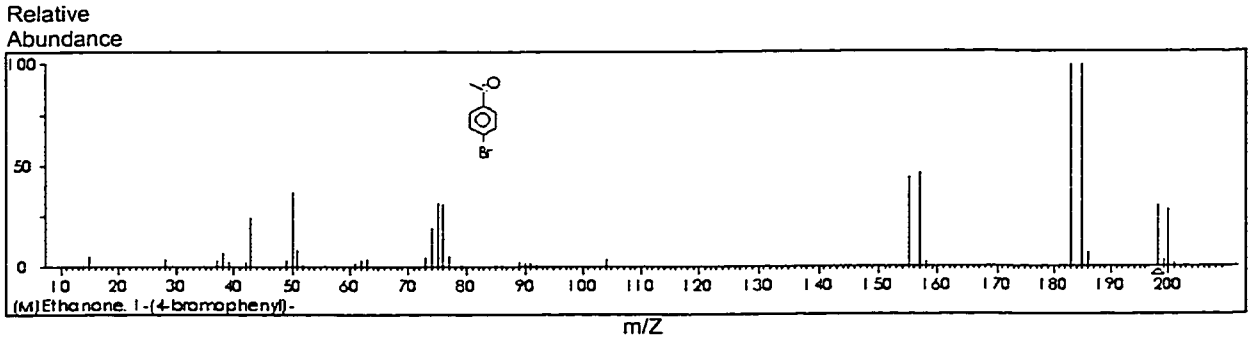
   MW: 198 CAS#: 99-90-1 NIST#: 118923 ID#: 78566
   Synonym:
   4'-Bromoacetophenone



LIST OF COMPOUNDS

9. 1-CHLORO-2,4-DIMETHOXYBENZENE
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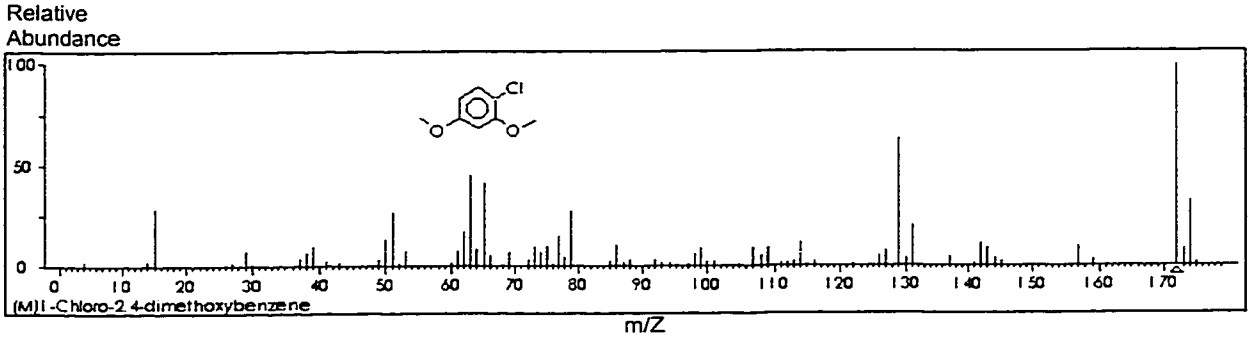
   MW: 172 CAS#: 7051-13-0 NIST#: 134497 ID#: 74909
   No synonyms



1. INTRODUCTION

1.1 Wood Smoke as a Pollutant

The use of wood as a renewable energy resource must be weighed against its air pollution potential. When wood is burned with a deficit of oxygen, products of incomplete combustion are formed (Larson and Koenig, 1994). If these by-products are not further oxidized, they cool and form fine particles rich in organic compounds of relatively high molecular weight. Many of these organic compounds, specifically some of the polynuclear aromatic hydrocarbons (PAHs), are carcinogenic and mutagenic. Outdoor concentrations of airborne chemicals resulting from wood combustion have been documented in a number of studies (Freeman and Cattell, 1990; Hawthorne et al., 1992; Hauk et al., 1994, Smith et al., 1993; Barrefors and Petersson, 1995). Larson and Koenig (1994) have summarized these study results (Table 1.1).

Table 1.1 lists many chemicals. However, the list is neither exhaustive nor truly reflective of the complexity of the overall chemical species present in wood smoke. Quantitatively, wood smoke is known to contribute from 20 to more than 70 percent of ambient suspended particulate matter concentrations depending on local conditions (Dasch 1982; Carlson, 1982; Chow et al., 1995; Cooper et al., 1981; Kowalczyk and Green, 1982; Murphy et al., 1984; Sexton et al., 1984). The size distribution of wood smoke particles is less than 10 μm with the majority in the 0.04-0.5 μm highly respirable range (Dasch 1982, Kamens et al. 1984, Kleindienst et al. 1986). The small particle size range is consistent with the fact that the majority of particulate mass is formed by condensation of unburned organic matter in the exhaust (Larson and Koenig, 1994).

Compared to natural gas or fossil fuel burning devices, conventional wood heating devices can have particulate and organic carbon emission rates 10 to 100 times higher magnitude (Cooper and Malek, 1982). The impact of wood smoke on ambient air quality has consequently become a concern in many regions. The carbonaceous portion, in particular, has attracted the most attention for two reasons: (1) because of its small size the particulate matter of smoke is capable of deep deposition in the human respiratory system; (2) its

Table 1.1 Chemical composition of wood smoke (Larson and Koenig, 1994)

Species[1]	g/kg wood[2]	Physical state
Carbon monoxide	80-370	vapour
Methane	14-25	vapour
VOCs (C_2-C_7)	7-27	vapour
Aldehydes	0.6-5.4	vapour
Formaldehyde	0.1-0.7	vapour
Acrolein	0.02-0.1	vapour
Propionaldehyde	0.1-0.3	vapour
Butryaldehyde	0.01-1.7	vapour
Acetaldehyde	0.03-0.6	vapour
Furfural	0.2-1.6	vapour
Substituted furans	0.15-1.7	vapour
Benzene	0.6-4.0	vapour
Alkyl benzenes	1-6	vapour
Toluene	0.15-1.0	vapour
Acetic acid	1.8-2.4	vapour
Formic acid	0.06-0.08	vapour
Nitrogen oxides (NO, NO_2)	0.2-0.9	vapour
Sulphur dioxide	0.16-0.24	vapour
Methyl chloride	0.01-0.04	vapour
Napthalene	0.24-1.6	vapour
Substituted napthalenes	0.3-2.1	vapour/particulate
Oxygenated monoaromatics	1-7	vapour/particulate
Guaiacol (and derivatives)	0.4-1.6	vapour/particulate
Phenol (and derivatives)	0.2-0.8	vapour/particulate
Syringol (and derivatives)	0.7-2.7	vapour/particulate
Catechol (and derivatives)	0.2-0.8	vapour/particulate
Total particle mass	7-30	particulate
Particulate organic carbon	2-20	particulate
Oxygenated PAHs	0.15-1	vapour/particulate
PAHs Fluorene	$4x10^{-5}$-$1.7x10^{-2}$	vapour/particulate
Phenanthrene	$2x10^{-5}$-$3.4x10^{-2}$	vapour/particulate
Anthracene	$5x10^{-5}$-$2.1x10^{-2}$	vapour/particulate
Methylanthracenes	$7x10^{-5}$-$8x10^{-3}$	vapour/particulate
Fluoranthene	$7x10^{-4}$-$4.2x10^{-2}$	vapour/particulate
Pyrene	$8x10^{-4}$-$3.1x10^{-2}$	vapour/particulate
Benzo(a)anthracene	$4x10^{-4}$-$2x10^{-3}$	vapour/particulate
Chrysene	$5x10^{-4}$-$1x10^{-2}$	vapour/particulate
Benzofluoranthenes	$6x10^{-4}$-$5x10^{-3}$	vapour/particulate
Benzo(e)pyrene	$2x10^{-4}$-$4x10^{-3}$	vapour/particulate
Benzo(a)pyrene	$3x10^{-4}$-$5x10^{-3}$	vapour/particulate
Perylene	$5x10^{-5}$-$3x10^{-3}$	vapour/particulate
Indeno(1,2,3-cd)pyrene	$2x10^{-4}$-$1.3x10^{-2}$	vapour/particulate
Benz(ghi)perylene	$3x10^{-5}$-$1.1x10^{-2}$	vapour/particulate
Coronene	$8x10^{-4}$-$3x10^{-3}$	vapour/particulate
Dibenzo(a,h)pyrene	$3x10^{-4}$-$1x10^{-3}$	vapour/particulate
Retene	$7x10^{-3}$-$3x10^{-2}$	vapour/particulate
Dibenz(a,h)anthracene	$2x10^{-5}$-$2x10^{-3}$	vapour/particulate

Table 1.1 cont.

Species[1]	g/kg wood[2]	Physical state
Trace elements		
Na	$3x10^{-3}$-$1.8x10^{-2}$	particulate
Mg	$2x10^{-4}$-$3x10^{-3}$	particulate
Al	$1x10^{-4}$-$2.4x10^{-2}$	particulate
Si	$3x10^{-4}$-$3.1x10^{-2}$	particulate
S	$1x10^{-3}$-$2.9x10^{-2}$	particulate
Cl	$7x10^{-4}$-$2.1x10^{-1}$	particulate
K	$3x10^{-3}$-$8.6x10^{-2}$	particulate
Ca	$9x10^{-4}$-$1.8x10^{-2}$	particulate
Ti	$4x10^{-5}$-$3x10^{-3}$	particulate
V	$2x10^{-5}$-$4x10^{-3}$	particulate
Cr	$2x10^{-5}$-$3x10^{-3}$	particulate
Mn	$7x10^{-5}$-$4x10^{-3}$	particulate
Fe	$3x10^{-4}$-$5x10^{-3}$	particulate
Ni	$1x10^{-6}$-$1x10^{-3}$	particulate
Cu	$2x10^{-4}$-$9x10^{-4}$	particulate
Zn	$7x10^{-4}$-$8x10^{-3}$	particulate
Br	$7x10^{-5}$-$9x10^{-4}$	particulate
Pb	$1x10^{-4}$-$3x10^{-3}$	particulate
Particulate elemental C	0.3-5	particulate
Normal alkanes (C24-C30)	$1x10^{-3}$-$6x10^{-3}$	particulate
Cyclic di- and triterpenoids		
Dehydroabietic acid	0.01-0.05	particulate
Isopimaric acid	0.02-0.10	particulate
Lupenone	$2x10^{-3}$-$8x10^{-3}$	particulate
Friedelin	$4x10^{-6}$-$2x10^{-5}$	particulate
Chlorinated dioxins	$1x10^{-5}$-$4x10^{-5}$	particulate
Particulate acidity	$7x10^{-3}$-$7x10^{-2}$	particulate

[1]Some species are grouped into general classes as indicated by italics.
[2]To estimate the weight percentage in the exhaust, divide the g/kg value by 80. This assumes that there are 7.3kg combustion air per kg of wood. Major species not listed here include carbon dioxide and water vapour (about 12 and 7 weight percent, respectively, under the assumed conditions).

carbonaceous nature enables it to retain toxic and some known carcinogenic and mutagenic organic substances. Evidence implicating inhalable airborne particles in a range of adverse health effects is mounting. As a result, many health authorities have recognized the urgency to assess the exposure and potential adverse health effects of wood smoke in impacted areas.

1.2 Background

In the early nineties, wood smoke studies undertaken in the Province of British Columbia (B.C.) generated a lot of publicity. In 1994, the B.C. Provincial Medical Health Officer concluded that "from a public health perspective, fine particulate air pollution is the most important outdoor air pollution in British Columbia...." (B.C. Environment, 1995). Two years prior to this statement, and in April 1992, the Minister of Environment, Lands and Parks had announced the intention to develop a plan, the *Clean Air Strategy*, to deal with the pressing air pollution situation. The B.C. government was also aware that wood smoke contribution to air pollution was significant. Since then, a series of measures had been implemented in the attempt to improve the ambient air quality. In 1993, the *Open Burning Smoke Control Regulation* was passed. In the same year, the *Wood Residue Management Policy* was adopted to phase out sawmill wood residue burners that had been a major source of air pollutants in B.C. On December 7, 1995, the provincial government took an additional regulatory step to eliminate these burners by passing the *Wood Residue Burner and Incineration Regulation* under the *Waste Management Act.*

Wood residue burners are not unique to BC; they are also found in two northern communities in Alberta. These Alberta communities have become concerned with the impact of wood smoke generated by these burners, and the potential adverse effects on human health. In particular, temperature inversions on calm, cold winter nights are known to limit vertical atmospheric dispersal; thus allowing wood smoke to accumulate near ground level (Cooper, 1980). Regional Health Authorities (RHAs) of these communities have been seeking technical support from Alberta Health, the provincial regulatory body, to perform health risk assessments with respect to wood smoke in their regions. The need for a feasibility study for an effective monitoring protocol was apparent.

2. LITERATURE REVIEW

In the past, environmental assessment on airborne particulate matter was almost exclusively based on ambient measurements of total suspended particles (TSP). Chang and Menon (1993) studied human respiratory airflow dynamics, and concluded that flow dynamics influence particle transport and areas of particle deposition within the respiratory system. Growing knowledge on particle aerodynamics, anatomy and physiology of the human respiratory system, furthermore, has shifted attention from TSP to finer particles.

2.1 Anatomy, Physiology and Particle Deposition

The anatomy and physiology of the human respiratory tract influence the airflow pattern and hence the deposition of inhaled aerosol and particulate matter. The human respiratory tract can be divided into three regions: the extrathoracic (head) region, the tracheobronchial (chest) region, and the alveolar region. The extrathoracic region is the upper respiratory tract that extends from the external nares to the larynx. In this region, the predominant particle deposition process is inertial impaction because of abrupt changes in the flow direction and resulting turbulence. Nasal hairs, turbinate (thin, scroll-like, bony or cartilaginous plates) of the nose and glottic aperture (throat opening) in the larynx efficiently remove large particles. The particles are then transported with the aid of mucus and eventually deposited into the gastrointestinal tract through gravity or the movement of cilia. Particles larger than 2.5 μm but smaller than 5 μm in aerodynamic diameter deposit in the tracheobronchial region, mainly by impaction and sedimentation (EPA 1982). Nevertheless, interception can also take place in this region depending on the size of particles. Sedimentation becomes more significant as the residence time increases, and as air velocity decreases. Fine particles <2.5 μm reaching the alveoli will deposit by diffusion and electrostatic attraction. A schematic representation of the five major particle deposition mechanisms in humans is illustrated in Figure 2.1.

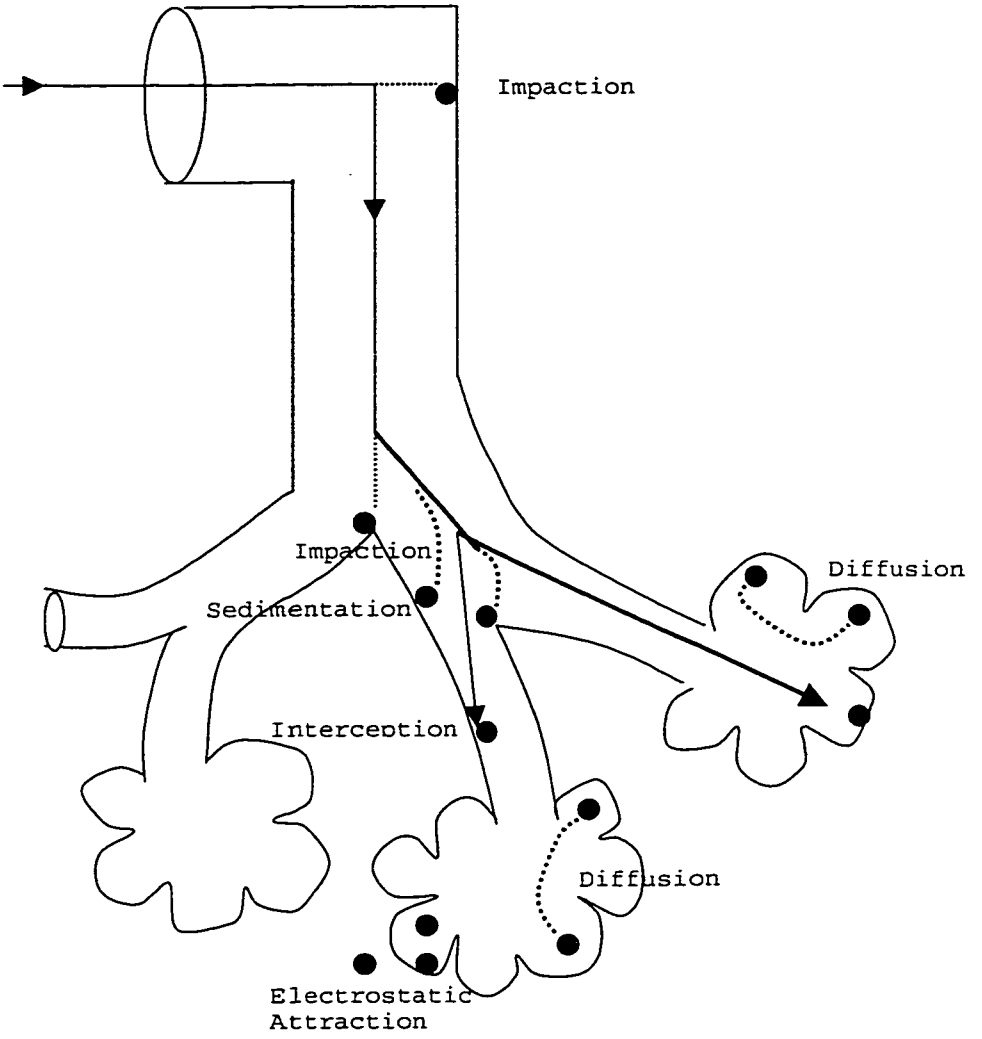


Figure 2.1 Schematic representation of five major particle deposition mechanisms in human (adapted from EPA, 1995)

2.2 Health Risk Assessment

Health risk assessment has been described as a four-step process (NAS, 1983; 1994) which includes hazard identification, dose-response relationship, exposure assessment and risk characterization. **Hazard identification** is the process of determining whether exposure to an agent, at any dose, is capable of causing an increase in the incidence of adverse effects. **Dose-response** defines the relationship between the dose of an agent and the probability of a specific adverse effect occurring. **Exposure assessment** evaluates the character and extent of uptake of an agent from the environment through various routes of exposure pathways. **Risk characterization** summarizes and interprets the information collected during the previous three activities and identifies their limitations and the uncertainties in the risk estimates (NAS, 1994). Integration of these four steps into a scientific process helps to determine the level of risk that in turn is used as a basis for public health policy consideration. The discussion of the health risk assessment process in this chapter will focus on the two steps that are the most relevant to this study, that is, hazard identification and exposure assessment.

2.2.1 Hazard Identification

Hazard identification is the first step in health risk assessment. It determines the causal relationship between a specific substance and resulting health effects. In airborne particulate matter studies, particles with aerodynamic diameters of less than 10 μm (PM_{10}) are of primary health concern. PM_{10} is subject to human alveolar deposition (Wolff et al., 1981). Consistent with the fact that the majority of wood smoke particles is formed by a condensation process in the exhaust (Larson and Koenig, 1994), wood smoke consists of large proportions of inhalable particulate matter with the majority falling into the 0.04-0.5 μm range (Kamens et al., 1983). The concern for these minute particles being respirable has led to PM_{10} air quality standards.

Evidence has indicated that fine particulate air pollution is associated with increased morbidity and mortality. However, the question of causality remains

unclear and is still under study (Dockery and Pope, 1994). Although some studies have noted that naturally produced particles, within a given particle concentration, have a small health impact for a given particle concentration due to their less toxic nature than particles of anthropogenic origins (Hefflin et al., 1994), other studies have found that size and mass concentration are important parameters in defining toxicity of particulate matter. For example, ultra-fine particles (<20 nm) have been found to be much more toxic than larger inhalable particles (Oberdorster et al., 1992; Driscoll and Maurer, 1991) possibly due to their origins and their larger surface area per unit mass which is available for chemical adsorption. While scientists continue this debate, the PM_{10} standard has become the first and only U.S. national air quality standard that is not based on specific chemical agents or class of chemicals.

Recent literature has provided a growing body of evidence implicating inhalable airborne particles in a range of health effects (Dockery et al., 1993; Ostro, 1993; Larson and Koenig, 1994). Extracts of wood smoke particulate matter have also been shown to have mutagenic activity (Bell and Kamens, 1986; Kamens et al., 1985; Kleindienst et al., 1986), and 10-25% of the mutagenicity may be attributed to particle-bound polycyclic aromatic hydrocarbons (PAHs) (Alfheim et al., 1984; Kamens et al., 1985). Other studies have established relationships between particle concentrations and health outcomes. These studies have shown that relationships between particle concentrations and measured health outcomes are remarkably consistent, regardless of chemical species (Brauer, 1995). Larson and Koenig (1994) have reviewed literature on wood smoke non-carcinogenic effects and suggest that wood smoke exposure in animals can disrupt cellular membranes, depress macrophage activity, destroy ciliated and secretory respiratory epithelial cells and cause aberrations in biochemical enzyme levels. Larson and Koenig (1994) have concluded that there is enough strength of association, consistency, temporality, plausibility, coherence, and analogy to suggest a causal relationship between elevated wood smoke levels and adverse respiratory health outcomes in young children.

2.2.2 Exposure Assessment

Exposure assessment is the quantification of the contact of an individual or a population with environmental pollutants. The International Union of Pure and Applied Chemistry Commission on Toxicology (1993) has defined exposure assessment as a process of measuring or estimating concentration or intensity, duration, and frequency of exposures to an agent present in the environment or, if estimating hypothetical exposures, that might arise from the release of a substance, or radionuclide, into the environment. Very often, investigators address air pollution concerns by the direct monitoring of the airborne pollutant mass concentrations in an impacted area. This approach is alluring because of its simplicity and speed in obtaining results. However, Hrudey et al. (1996) have noted that the exposure assessment process encompasses not only the exposure concentrations, but also the identification of sources. They define exposure assessment as a process of seeking qualitative insight and/or quantitative data on the magnitude of human exposure to xenobiotics, exposure duration and frequency. In their definition, Hrudey and his colleagues also include the identification of pollutant sources, routes of exposure and the characteristics (size, nature and class) of the potentially exposed population as components of exposure assessment. Without the identification of the pollutant source(s), developing a comprehensive risk management strategy to protect the health of the public would not be possible. The direct measurement approach may provide some numerical data for discussion, but data of this nature merely indicate the quantity of some airborne pollutants. However, risk management will require knowledge of the source of airborne pollutants in order that appropriate emission controls can be implemented.

2.2.2.1 External Exposure as a Surrogate

The exposure process takes place in a continuum ranging from sources and exposure pathways to measurement of cellular adducts or metabolites, and to biomarkers of effects (Hulka and Wilcosky, 1988). Therefore, an exposure assessment distinguishes between external exposure, internal exposure and

biological effects. The most direct information for exposure assessment, is undoubtedly the internal exposure, that is, the concentration of the toxic agent at the critical target organ. Internal exposure is best measured by determining the concentration of the toxicant or its ultimate metabolite(s) at the critical site in the target organ or by determining its adducts with cellular macromolecules (Greim et al., 1995). The reference of internal exposure, external exposure can be extrapolated and used as a surrogate for the internal exposure. However, factors of influence including bioavailability of the chemicals, variations in concentrations and routes of exposure, physical activity, and individual variation in metabolic rates, distribution and excretion must be carefully considered in the assessment process.

A person's daily activity can provide insights into an individual's external exposure to an environmental pollutant. Likewise, to characterize a population's external exposure, the population's exposure profile must be known. A population exposure profile is the record of exposure as a function of time throughout the day in specific locations, and of the range and distribution of time-activity within the population. In this type of study, the statistical survey design techniques of the social scientist and the measurement technology of the chemist and engineer are combined to determine the exposure profile (Ott, 1985).

Two such time activities studies have recently been completed in North America. Between 1993 and 1994, a large scale survey based on interviews with 9,386 respondents in the U.S. found U.S. residents on average spend 87.2% of their time indoors, and 5.6% outdoors (Robinson and Nelson, 1995). A similar Canadian study (Leech et al., 1996) was carried out in Toronto, Vancouver, Edmonton and Saint John in 1994/1995. As expected, the study also confirmed that Canadians spend the majority of their time indoors (88.6%). Data from both studies support earlier observations of Spengler et al. (1990) and Smith (1993) that indoor exposure, not ambient concentrations, is the most important consideration in an assessment process of air pollution exposure.

2.2.2.2 Ambient Concentration as a Surrogate

A person's external exposure to a pollutant is most accurately reflected by characterizing one's total contact with the specific pollutant via various exposure pathways. Such a concept has been termed the "total exposure assessment" by Ott (1985). However, personal exposure monitoring is not always feasible due to cumbersome monitoring equipment and the lack of willing participants. The indoor monitoring of individual homes also can be expensive and time-consuming. Some studies require extended sampling periods in order to collect sufficient quantities of pollutants for various analyses. In such a situation, a lengthy sampling period may distort the concentrations of pollutants in any relatively small and confined space rendering monitoring inaccurate. Alternative approaches must therefore be investigated.

Outdoor and indoor pollutant concentrations can be reconciled. Indoor concentrations of many pollutants are known to be driven by ambient concentrations (Colome et al., 1992) that indoor pollutants with outdoor origins correlates with the outdoor/indoor exchange rate. Researchers (Koutrakis et al., 1992; Larson and Koenig, 1994) have demonstrated that by determining the penetration rate, the indoor pollutant concentration can be predicted based on the ambient concentration contributed by an emission source, and hence estimated human exposure characterization is possible without personal exposure monitoring. By incorporating data from studies such as the *Canadian Human Activity Pattern Survey* by Leech and co-workers (1996), the average indoor exposure to the pollutant of the Canadian population can be characterized.

Ambient measurements alone, in practice, provide poor prediction of personal exposure. One study has found less than 1% of the variance in personal exposure was explained by the outdoor respirable particulate measures (Spengler et al. 1985). However, using the outdoor concentration to estimate a population's exposure to a pollutant may still be valid. In order to provide better prediction, ambient concentrations must be used in combination with the population's activity profile, outdoor concentration of the pollutant, outdoor/indoor

air exchange rate, and infiltration rate of the pollutant. With consideration of other influencing factors such as bioavailability, variations in concentrations and routes of exposure, physical activity, and individual metabolic rates, distribution and excretion, the internal exposure can in turn be delineated.

2.3 Modelling

A complete knowledge of pollutant sources, chemical profile, and the human receptor's exposure to a pollutant is needed to perform an effective health risk assessment. However, our scientific knowledge about these components is not balanced. While much knowledge has been accumulated on the identification and health effects of pollutants, our knowledge of actual human exposure to pollutants of specific sources is often rudimentary (Ott, 1985). Without compiling complete data on pollutant sources, chemical profile, and the human receptor's exposure to the pollutant, a comprehensive health risk assessment is not possible.

Knowledge of pollutant source apportionment is essential in improving our performance in assessing human exposure. For instance, it is known that ambient inhalable particulate matter has multiple sources. These sources include biomass burning, fossil fuel combustion, geological sources, farming and many other natural and anthropogenic activities. In order to determine the impact of a single pollutant such as wood smoke, and to assess the level of human exposure, and ultimately devise an appropriate risk management strategy, pollutant sources must be identified and differentiated from each other. These pollutant sources can then be managed accordingly in order to protect the health of the public. The mere detection and quantification of pollutants present in the environment may be insufficient to develop an effective risk management program.

The quantitative impact of different emission sources on a region can be determined with various air quality models. The dispersion model has been the traditional method employed in source apportionment studies. Recently, advances in the design of air quality monitoring equipment and laboratory

analysis techniques have resulted in the increased popularity of the receptor model. These choices are described in subsequent sections. However, unlike dispersion models, receptor models are often unable to apportion the impacts of specific sources from the same source groups due to the similarity of chemical compositions (Freeman et al., 1989). Also, receptor models are not capable of predicting the impacts of a proposed source (Gordon, 1988). In spite of these limitations, receptor models have proven to be a valuable tool for local source apportionment where few complex sources exist and where the major sources have well-defined emission profiles (Ward and Hardy, 1989). The US Environmental Protection Agency (EPA) has recommended both source and receptor models to quantify the contribution of major pollution sources at a particular area (US EPA, 1987a).

2.3.1 Dispersion Model

The dispersion approach is based on a mathematical model coupled with meteorological information, and on emission source information of the pollutant (Lewis and Einfeld, 1985). The source models are most useful when emission sources have been already identified and emission rates are known. Emission inventories for various sources are used as inputs for plume, box, or grid models to predict ambient concentrations of air pollutants. However, Watson (1988) has been critical of dispersion modelling because its accuracy is highly dependent on emission profiles that are often unreliable, and because models are constrained in areas where emission sources are sporadic and where emission rates fluctuate at various times of the day. One example is automobile emissions. The application of source models can also be complicated with unstable meteorological conditions due to geography and other factors.

2.3.2 Receptor Model

Increasingly it is recognized that receptor modelling using tracer species can provide a viable and cost effective alternative for the identification and apportionment of airborne contaminants. The term "receptor modelling" refers to

a group of source-apportionment techniques. In contrast to dispersion models, receptor models depend on the chemical and physical analysis of substances of interest collected at a given site; it is thus distinguished from dispersion models (Friedlander, 1984), which require information at the source of emissions, and the consideration of meteorological conditions. As a receptor model assesses the contribution from sources using measurements made at the site of impact, source information and meteorological information are of secondary importance (Lewis and Einfeld, 1985). Various receptor-oriented models have been developed to apportion source contributions to ambient air pollution (Cooper and Watson, 1980; Currie et al., 1984; Thurston and Spengler, 1985; Wang and Hopke, 1989). The two most common types of receptor models are chemical mass balance (CMB) and multivariate analysis (Nitta et al., 1994).

Regardless of types, mass conservation is the basic assumption of all receptor models (Thurston and Lioy, 1987). For example, if p are the existing sources, and if there is no source emissions interaction causing mass removal or accretion, then the total pollution mass measured at a receptor (M) is the sum of all the individual sources contributions (S_j).

$$M = \sum_{j=1}^{p} S_j \qquad (1)$$

Miller et al. (1972) shows that the concentration of an investigated chemical property at the receptor site can be expressed as:

$$C_i = M \quad a_{ij} \quad f_{ij} \qquad (2)$$

or,

$$C_i = \sum_{j=1}^{p} S_j \quad a_{ij} \quad f_{ij} \qquad (3)$$

where f_{ij} is the mass fraction of source contribution j possessing property i in the source emission;
a_{ij} is the coefficient of fractionating of property i between the source and receptor.

The fractionating coefficient a_{ij} accounts for the effects of transformation or accretion in the atmosphere between the source and the receptor. Its value thus varies with source type, location, time, ambient conditions and many other factors. Most applications of Equation (2) in source apportionment assumes a_{ij} = 1.0 over short transport distances. That is, it is assumed that mass fraction of source is added or lost at a rate equal to that of the pollution mass as a whole (conservation of f_{ij} characteristics). This assumption presents limitations in using receptor modelling to estimate source impact on a receptor site that requires long distance transportation. Figure 2.2 summarizes various processes that would compromise the a_{ij} = 1.0 assumption (Cooper, 1981).

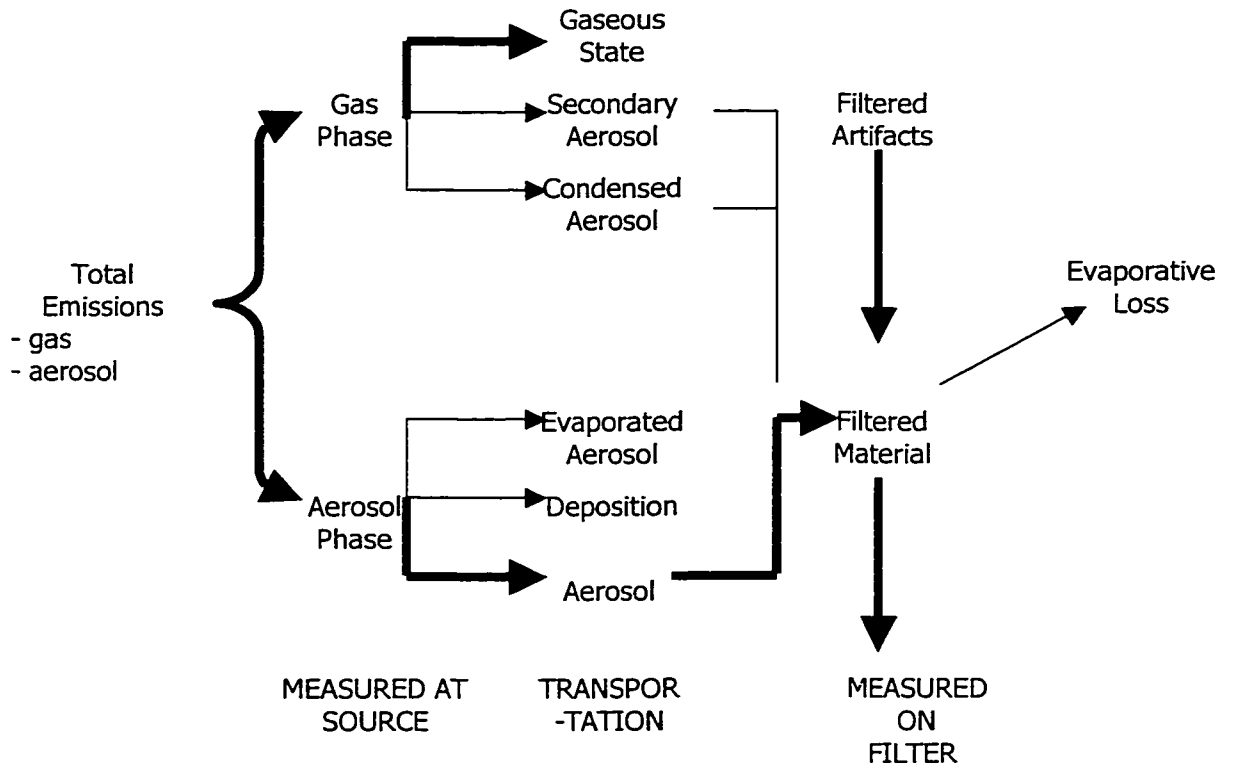


Figure 2.2 Factors influencing particle fractionation and accretion between source emission and receptor (adapted from Cooper, 1981).

2.4 Tracers

All receptor models require knowledge of chemical species exclusively associated with the pollutant of interest. These chemicals, called unique tracers, are useful in identifying the pollutants and their impact on an airshed. To date, most receptor modelling has been focused on elemental tracers because of their stability. Elemental tracers have been successfully used in atmospheric studies to identify pollution sources. For example, vanadium (V) and nickel (Ni) are indicators of oil combustion; airborne lead (Pb) in urban areas was a good indicator for motor vehicles exhaustion before unleaded gas was introduced; sulphur (S), selenium (Se), and arsenic (As) are often associated with coal-related pollution. In spite of some complication due to differential sedimentation or dissolution of these stable species, the calculation is fairly uncomplicated. The use of volatile and reactive species has not been popular because of their instability and the potential of transformation during the transportation process from source to the receptor site. The presence of hydroxyl radical, reactive gases such as ozone, and the nature of substances on which they adsorb can all affect the degradation half-life of an organic substance (Howard et al., 1991). Kamens and co-workers (1986; 1987) studied the reaction rates of PAHs associated with fresh wood soot and reported that the ambient air temperature played a role on the reaction rate of PAHs. At 20 °C, PAH half-lives were typically 30-60 minutes, but at 7 °C, half-lives of same substances increased to several hours or even days.

Theoretically, wood combustion by-products reviewed by Larson and Koenig (1994) in Table 1 all have the potential to be used as tracers for estimating the quantitative contribution of wood smoke to ambient air pollution. Previous attempts have been made to use chemical species such as NO_x, HCN, CH_3CN, CH_4, saturated C_2 - C_5 hydrocarbons, CO and CO_2. However, these chemicals have been proven to be unsuitable because macro-molecular smoke particles are difficult to characterize, and the gaseous emissions such as NO_x, CO_2, and PAHs have too many non-wood smoke sources (Simoneit et al., 1993). Other by-products have also been proposed, tested and used to various degrees

of success as tracer species for wood smoke in various studies, including:

- radiocarbon (^{14}C)
- potassium (K)
- methyl chloride (CH_3Cl)
- retene (1-methyl-7-isopropylphenanthrene)
- levoglucosan
- methoxylated phenols (guaiacol and syringol derivatives)

However, each of these tracers has its advantages and disadvantages. The following is a brief discussion of each potential tracer.

2.4.1 Radiocarbon (^{14}C)

Wood smoke has a high concentration of carbonaceous particles. Therefore, carbon isotopes are potential tracers. Currie (1982) determined the relative amounts of particulate carbon from contemporary (e.g., wood) and fossil fuel carbon combustion sources by means of the $^{14}C/^{12}C$ ratio. The distinction between the two is possible because contemporary (new) carbon contains trace amounts of ^{14}C, but fossil fuel carbon is essentially devoid of ^{14}C. Carbon isotopes are effective tracers because they provide direct quantification. Hence, they are called the *absolute* (calibrated) *unique tracers*. Unfortunately, the procedure is expensive and the required analytical instruments (accelerator mass spectrometers) are scarce.

The use of radiocarbon has recently been under scrutiny. Hawthorne et al. (1992) have suggested that approximately 20% of atmospheric radiocarbon may come from cooking of animal fats and other biogenic sources. In 1994, a research team led by the original proponent of radiocarbon as wood smoke tracer (Currie et al., 1994) also reported an increased quantity of radiocarbon of unknown origin in night-time air samples. It was postulated that excess particulate radiocarbon could be "recycled" carbon condensing from daytime volatile organic carbon to form particulate matter at low night-time temperature. Consequently, the accuracy of using radiocarbon is being re-considered and the effects of volatile carbon condensation at night-time are being examined. These

considerations call into question the status of radiocarbon as an "absolute" tracer.

2.4.2 Potassium (K)

Potassium has been a major tracer species in recent wood smoke studies. Analysis using potassium (K) is less expensive than radiocarbon analysis, and it has the advantage of being a stable elemental tracer. But, unlike original expectations for radiocarbon, it is not an *absolute* (or calibrated) tracer for wood smoke. One of the problems associated with the use of potassium is its abundance in the earth crust - it is present in wind-blown soil that generally constitutes a significant fraction of total suspended particulate matter in the atmosphere. Several studies have found that soil typically contributes 10-50 percent of the TSP in urban areas (Cass and McRae, 1983; Friedlander, 1973; Kleinman et al., 1980; Cooper and Watson, 1980; Gordon, 1980; Kneip et al., 1983). In order to use potassium as a tracer effectively, correction for soil potassium is needed. However, the correction process requires knowledge of or at least a reasonable assumption regarding the potassium concentration in local soil (Lewis and Einfeld, 1985).

A second problem associated with using potassium as a tracer is that its production by wood combustion may exhibit high variability. Stiles (1983) observed substantial variations in potassium concentrations during the burn cycle of different types of wood. Potassium concentration from burning pine was much lower than that for the hard woods. The use of potassium as a tracer for accurate wood smoke apportionment, therefore, relies heavily on the knowledge of the wood types predominantly used in the region, of the proportions, and on an assumed average burn-rate.

In spite of these concerns relating to the use of potassium as a tracer, Currie et al. (1994) have maintained that mineral-corrected potassium is a reliable, cost-effective tracer for wood-burning carbon aerosol.

2.4.3 Methyl Chloride (CH_3Cl)

The analysis of methyl chloride (CH_3Cl) is inexpensive and experimentally simple (Khalil et al., 1983). However, the high and seasonally variable concentration of CH_3Cl in the background from other atmospheric sources renders it an ineffective tracer for wood smoke. Its accuracy is unlikely to be better than ± 50% (Khalil et al., 1983). Compared to soil-corrected potassium, the signal to background ratio for methyl chloride is at least one order of magnitude smaller, and it has the further uncertainty of being a gaseous tracer for fine-particles (Lewis et al., 1988).

2.4.4 Retene (1-methyl-7-isopropylphenanthrene)

Laflamme and Hites (1978) first proposed the abietic acid to retene conversion in wood tissue under combustion conditions. Simoneit and Mazurek (1982) proposed a similar reaction scheme. Ramdahl et al. (1984) proposed using the compound as a marker for softwoods. Since abietic acid is present in high concentrations in pine wood resin, retene would presumably be present in airborne particulate matter from a region influenced by wood burning where soft woods were used as fuels. Overall, retene appears to be a more specific tracer than methyl chloride. Unfortunately, however, its absence in hardwood combustion renders it unsuitable for studying hard wood combustion (Lewis et al., 1988). Therefore, its use as a tracer has been restricted to areas predominantly burning softwood. The much greater analytical costs (compared to potassium) often discourage its consideration (Lewis et al., 1988). Moreover, the suggestion by Steiber and Dorsey (1990) that any fuel rich in aromatics will produce condensed-ring aromatics including, under the right flame conditions, retene has raised doubts regarding its validity as a wood smoke tracer.

2.4.5 Levoglucosan (anhydride of β-glucose)

Levoglucosan is a sugar characteristically produced in trees. Its natural origin and absence in anthropogenic and background sources have sparked interest in using it as a tracer (Hornig et. al., 1983). Under normal wood stove

conditions, levoglucosan is present in the particulate emissions. However, transformation to other by-products during pyrolysis is possible and this would generally lead to an underestimation of wood smoke contributions in source apportionment. The use of levoglucosan as a wood tracer may be unreliable.

2.4.6 Methoxylated Phenols

Methoxylated phenols (guaiacol and syringol derivatives) were first proposed as wood smoke tracers by Hawthorne and colleagues (1988, 1989, 1992). The North Dakota team asserted that the average total concentrations of guaiacol species in wood smoke (per unit weight of inhalable particulate carbon), were consistent regardless of wood type, and syringol species were consistent in wood smoke originated from hardwood. They compared apportionment results obtained with the ^{14}C method, and results were well correlated.

A study was carried out in three stages. In 1988, the team initially identified thirty methoxylated phenols in unfractionated methylene chloride extracts of soot from residential wood stoves. While the majority of methoxylated phenols were associated with the particulate matter, some of them were primarily in the vapour phase. The team suspected that these methoxylated phenol species could be potential tracers for atmospheric wood smoke pollution.

In 1989, Hawthorne and colleagues collected samples of particulate- and vapour- phase organic compounds from 28 wood stoves and fireplace smoke plumes using quartz filters and polyurethane foam (PUF) sorbent plugs. The result revealed that concentrations of guaiacol derivatives per weight of particulate carbon were consistent in both hardwood and softwood. In contrast, concentrations of syringols derivatives were only consistent in hardwood smoke. The Hawthorne team was confident that guaiacol derivatives were useful tracers for wood smoke pollution.

In 1992, the team used their 1989 methoxylated phenols-based smoke signature to apportion wood smoke in six different locations in Minneapolis, MN, and Salt Lake City, UT. The apportionment results were compared to results using the ^{14}C analysis and were found to have excellent correlation (r^2 = ca.

0.90). Hawthorne et al. then concluded that the measurement of airborne methoxylated phenols (smoke signature) could be used to determine the fraction of PM_{10} particulate carbon contributed by wood combustion. Because the sum of major guaiacol species correlated well with total guaiacol species, they suggested that it was sufficient to use the sum of guaiacol and the 2 major derivatives, 4-methyl-guaiacol and 4-ethyl-guaiacol, instead of the total sum of all guaiacols. This method would only require the extraction of the PUF sorbents. The extraction of particulate matter could be eliminated.

Another research team (Steiber and Dorsey, 1990) also attempted to use methoxylated phenols as a wood smoke tracer. Their study data monitored at three sites, including the emission stack, provided circumstantial evidence of transport stability for methoxylated phenols. The correlation coefficients for the stack and the two receptor sites were very similar at 0.89 and 0.87.

Based on the foregoing review, methoxylated phenols appear to offer the most promise for tracers that could be used for inhalable particulate carbon source apportionment. Accordingly, the findings of Hawthorne and colleagues (1988, 1989, 1992) and Steiber and Dorsey (1990) have been summarized in greater detail. While both teams have suggested that methoxylated phenols are the best class of compounds to use as wood smoke tracers; the use of these tracers has not been validated by other workers.

3. HYPOTHESIS AND STUDY OBJECTIVES

3.1 Hypothesis

Based on the work of Hawthorne et al. (1988, 1989, 1992) and of Steiber and Dorsey (1990) methoxylated phenols are a feasible tracer group for wood smoke particulate carbon.

3.2 Objectives

It was the objective of this study to identify and recommend to Alberta Health a methodology that would be both economically and technologically feasible in Northern Alberta for wood smoke source apportionment. As described in the previous chapter, many methodologies have been proposed and used by investigators to attribute the contribution of wood smoke to inhalable particulate carbon in ambient air. However, it is recognized that not all of these methods are available or effective in the region. Radiocarbon undoubtedly is the most accurate tracer for source attribution, but, the method is expensive and the analytical instrument for radiocarbon is not available in Alberta. The use of potassium was considered. Analytical instruments for potassium were more readily available, but the effectiveness of this methodology depended on accurate knowledge of local soils chemistry. Based on the literature review it appeared that methoxylated phenols were the most promising alternative tracer species.

3.2.1 Validation of Tracer Modelling

Regardless of the nature of the tracer species, the validity of the receptor/tracer model rests upon a number of important assumptions, which Currie et al., (1994) have summarized:

- The receptor model is a linear model in which tracers are conservative. The fate, transport and distribution of a chemical released into the environment are often not well understood. An assumption of mass conservation is required.
- Source identity is known.

- System under study is a closed one - aerosol from sources outside the studied air shed and conveyed by long-range transport is not considered.
- Unique tracers are specific to the sources in question, and representative for the material being traced. For example, carbon isotopes are directly associated with source carbon (or selected compounds); markers such as potassium and methoxylated phenols are indirect tracers which are assumed to be representative of source carbon.

3.3 Tracer Selection Rationale

3.3.1 Stability

Methoxylated phenols appear to be suitable candidates to trace wood smoke. An important factor that determines the success of organic tracers is their stability in ambient air while being transported from source to the receptor site. Although no studies of methoxylated phenols have been done, the low winter ambient temperature in Alberta is expected to help to promote the stability of airborne organic compounds. To date, most reactivity studies on organic compounds have been concentrated on PAHs. Kamens and co-workers (Kamens et al. 1986; Kamens et al., 1987) have reported that the ambient temperature has a dramatic effect on PAHs reactivity, and Nielsen et al. (1983) have found that the loss of PAHs in low ambient temperature due to reactivity is negligible. At this time, no information on the degradation half-lives of methoxylated phenols in the environment is available in the literature. However, circumstantial evidence provided by Steiber and Dorsey (1990) and more recently by Hawthorne et al. (1992) suggests that this tracer group is relatively stable, at least in winter.

3.3.2 Uniqueness

Another important factor is the uniqueness of the methoxylated phenols. As a group, methoxylated phenols (guaiacol, syringol and their derivatives) in airborne particulate matter are unique to the burning of wood because they are a direct consequence of the thermal destruction of the lignin structure (Steiber et

al., 1992). Wood is made up of approximately 30 weight percent lignin, which is a skeletal network of branch-chain polymers that provide structural integrity, and of small amounts of resinous material and inorganic salts. The lignin polymer consists of two main monomers, a guaiacyclo-propane structure and a syringyl-propane structure. Upon heating, these structures break apart, which produces a large variety of smaller molecules, many of which are part of the general class of oxygenated monoaromatics (Steiber et al., 1992) including methoxy-phenols.

3.3.3 Availability of Analytical Instruments

Another obvious advantage of using methoxylated phenols over radiocarbon is that their analyses can be performed with conventional GC/MS instruments which are widely available in environmental laboratories.

3.4 Rationale of Selecting Guaiacols as Tracers

In this study the use only of guaiacol and derivatives as tracers was investigated. The decision not to include syringols in this study was based on the following considerations:

- Hawthorne et al. (1989) have suggested that while guaiacol derivatives are useful in tracing wood smoke of both hardwood and softwood, the production of syringols during softwood combustion is not significant. Indigenous trees in Alberta used as combustion wood include both hard- and soft- wood species. The majority of wood burned in wood residue burners, however, is softwood, so the use of guaiacol derivatives as tracers appears to be more useful for detecting this source.
- The decision was also based on the consideration that syringols were not found in all types of wood. Only hardwood burning would emit significant concentrations of syringols (Hawthorne et al., 1989). Moreover, the stability of syringol and its derivatives was questionable. Hawthorne et al. (1992) observed that due to different volatility, most syringol derivatives were collected in the particulate filter extracts. Their association with particulate matter might enhance the degradation process. Hawthorne and co-workers

(1992) suggested that the presence of an additional methoxy group on syringol derivatives might result in increased reactivity. As a result, the feasibility of syringols was not investigated in this study.

While several major species of methoxylated phenols were used in this study to determine the smoke chemical profile, they were grouped together and assessed as one single entity. Conservation of tracers was assumed in that the chemical profile of smoke (micrograms of methoxylated phenols per milligram of inhalable carbon) remained the same at the source and at the receptor site. Possible chemical transformation during the transportation process was not considered. However, the sampling was done in the exhaust stream of the wood burning source so there was only minimal reaction time available for decomposition of methoxylated phenols.

4. METHODOLOGY

In order to achieve the study objective, data were generated to determine the smoke profile of firewood at the source. Four different types of wood that are indigenous to Northern Alberta were chosen to burn. The inhalable particulate and the volatile organic carbon portions in the smoke were collected simultaneously to determine the smoke chemical profile(s). In turn the smoke signature was assessed to determine the feasibility of using organic tracers for source apportionment. A preliminary sampling run (Phase I) was performed on April 13 and 14, 1997. The first set of data demonstrated both intra- and inter-specific variability amongst different wood species. However, the results observed were not conclusive because of the small sample number (n). As a result, a second run (Phase II) with a larger sample number was necessary in order to establish an adequate confidence level in the interpretation of results. Several logistical details determined the scheduling. An immediate re-sampling in 1997 was not possible because of the rising ambient temperature as spring was approaching. Phase II was eventually carried out on February 18-21, 1998, during which the sample number (n) was increased to 10 for each wood type. Improved analytical capability was also provided by the availability of a new gas chromatograph - mass spectrometer (GC-MS).

4.1 Sampling Train, Smoke Generation and Collection

This study involved the burning of 4 types of wood indigenous to the area: birch, poplar, pine and spruce. The following information describes the sampling train assembly, smoke generation and signature collection protocol, pre- and post- sampling gravimetric analyses of particulate filters, determination of carbonaceous portion in the collected PM_{10}, pre-sampling preparation of polyurethane foam filters (PUFs), quantification and identification of methoxylated phenols using GC/MS, and the determination of the smoke signatures.

Where Signature = mass of total guaiacols/mass of total particulate carbon

For example, the Phase II smoke sample Pine #6 contains 19 μg of total guaiacols, and the weight of inhalable particulate carbon collected simultaneously was 0.53 mg. The signature (calibration factor) of this pine smoke sample was 35 μg/mg.

Gravimetric analysis and total carbon determination were performed at the Alberta Research Council (ARC, Vegreville, Alberta), while the GC/MS analyses were performed at the Environmental Health Sciences Laboratory, University of Alberta.

A prototype particulate matter collection device was on loan from Alberta Health. To facilitate this study, modifications were made to the collection train to allow a simultaneous collection of volatile methoxylated phenols. The modified sampling train included an in-line arrangement of a Marple PEM200 PM_{10} impactor, a polyurethane foam sorbent, and an air pump. Between the impactor and the polyurethane foam sorbent, teflon tubing was used to avoid possible contamination of the PUF from off-gassing of other materials. Prior to the actual sampling, the sampler collection efficiency was evaluated using a co-location sampling protocol alongside a U.S. Environmental Protection Agency (US EPA) referenced Dichotomous PM monitor at an Alberta Environment and Protection (AEP) air monitoring station in NW Edmonton, Alberta. The protocol has been described elsewhere (US EPA, 1987b).

4.1.1 PM_{10} Monitor

A Marple Personal Environmental Monitor (PEM 200) was used to collect inhalable particulate matter (Plate 4.1).

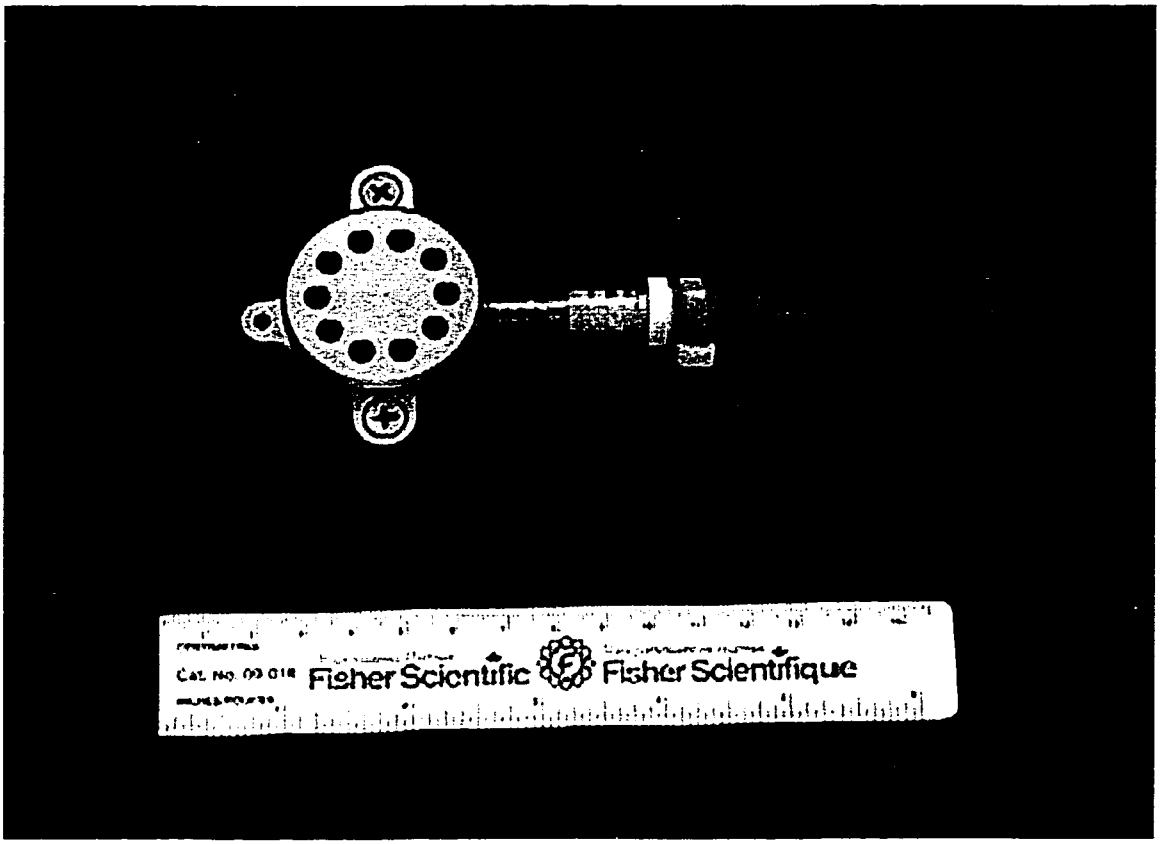


Plate 4.1 Marple PEM 200 Impactor

The monitor was a single stage impactor equipped with a quartz after filter. Its operation is based on the inertial separation of airborne particles using a conventional impactor as described by Marple and Liu (1974). As air accelerates through a number of nozzles inside the device, it impinges upon a plate. Airborne particles larger than 10 μm aerodynamic diameter were collected on the impaction plate due to their inertia across the air streamlines, and these oversize particles were discarded. Smaller particles were carried along the air streamline and were collected on the quartz after-filter for gravimetric analysis and quantification of total carbon. A flow-rate of 10 LPM (litre per minute) was maintained with a calibrated air pump so as to optimally maintain the 10 μm cut-point. The impactor consisted of 3 basic parts: cover, impaction plate assembly and base. Ten round nozzles were located in the cover. A schematic diagram of the monitor is provided in Figure 4.1.

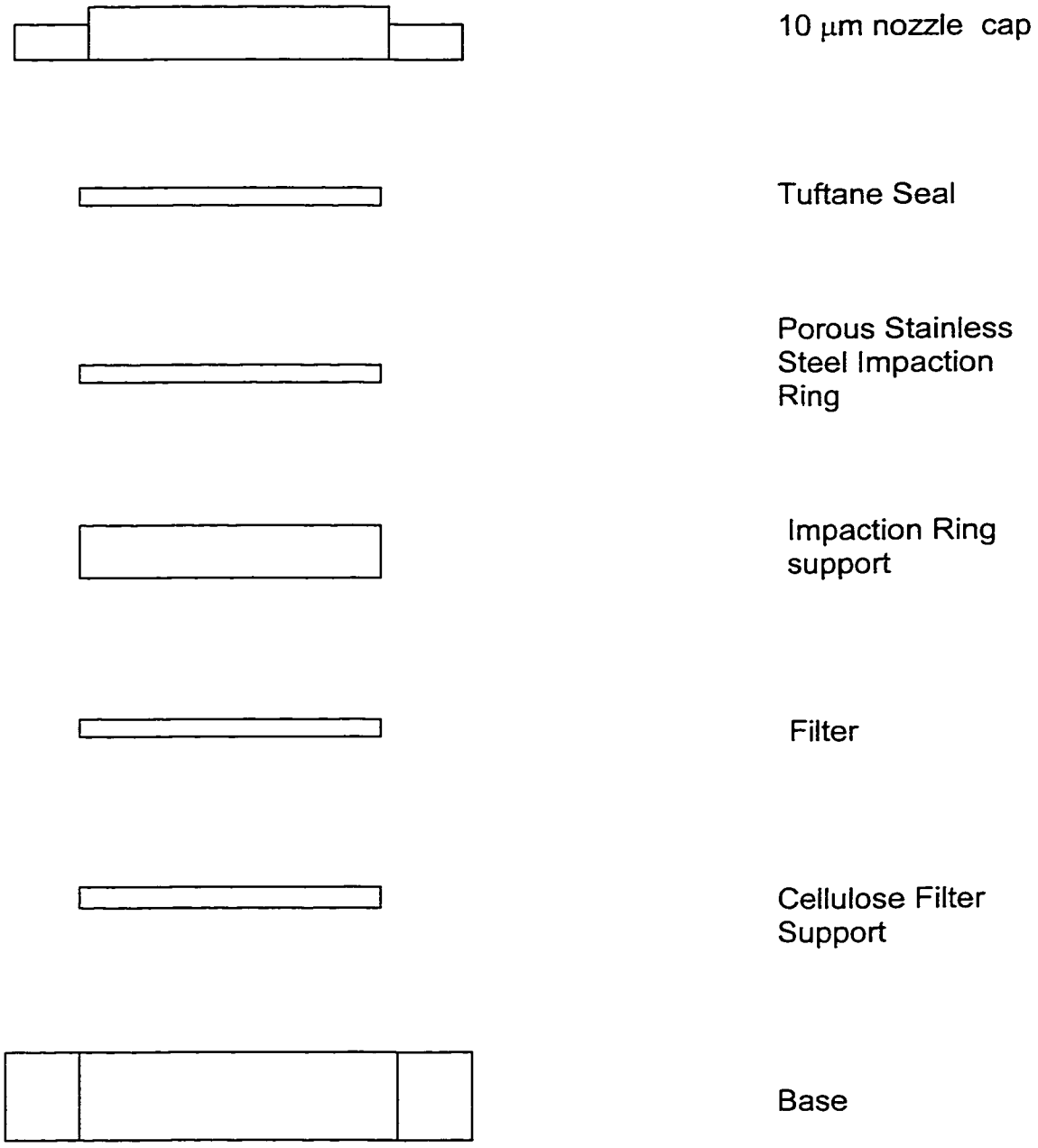


Figure 4.1 A Schematic Diagram of Marple PEM Impactor

4.1.1.1 Impactor Plate Assembly

The surface of the impactor plate was saturated with a light mineral oil. This oiling procedure provided a sticky surface that minimized oversize particles from bouncing off and collecting on the after filter, which would affect the accuracy. The manufacturer recommended cleaning and removing particles from the plate after every use. However, when the plate was checked visually after a 15-minute sampling, very little or virtually no deposit visible on the plate, possibly because the size range of wood smoke particulate matter was primarily <10 μm. The impactor plate was washed with a soap solution after every 10 sampling runs.

4.1.1.2 Quartz Filter

The Marple impactor was fitted with a pre-fired 37-mm quartz after filter (URG, NC) to collect inhalable particulate matter. Pre-fired quartz filters were selected for the collection and quantification of total inhalable carbon using the combustion method because they have a low background carbon content, high collection efficiency, and are chemically inert at high temperature.

4.1.1.3 Cellulose Support Filter

A cellulose support filter (SKC, PA) was placed in the base under the after filter to provide support and aid in forming a seal between the filter and base.

4.1.2 Polyurethane Foam Sorbent (PUF)

The collection efficiency of vapour-phase guaiacols depends on the absorbent. An effective absorbent must be able to effectively trap the methoxylated phenols, maintain an adequate flow-rate, and be able to withstand the severely cold temperature in the sampling region. Several materials were considered for these criteria. Reference was made to the work of Guenther (1987), which stated that strong binding between volatile PAHs and the activated carbon resulted in very poor recovery efficiencies when extracting for analysis.

Tenax and XAD-2 are also effective sorbents for volatile organic compounds; however, they tend to ice up in extremely cold temperatures, which affects the flow-rate. Consequently, this study followed the choice of the North Dakota team (Hawthorne et al., 1992), that is, polyurethane foam sorbent.

In Phase I (April, 1997), one polyurethane foam (PUF) sorbent plug and a small half PUF (URG, NC) were placed in series in the glass holder (Plate 4.2), which was fitted in-line between the Marple impactor and the air pump to collect vapour-phase guaiacols and derivatives (Hawthorne et al., 1989; 1992). According to the supplier, these PUFs were each sufficient for a 24-hour sampling period with an ambient airflow of 15 LPM. Putting a second PUF in place ensured no loss of guaiacol and derivatives even in the event of overloading and breakthroughs of the front full PUF. However, post-sampling analysis of a small PUF in series with an overloaded particulate filter (Sample Birch 1) indicated that guaiacol and derivatives were not detected in the second PUF. Thus, the half PUF in series was deleted in Phase II (February, 1998).

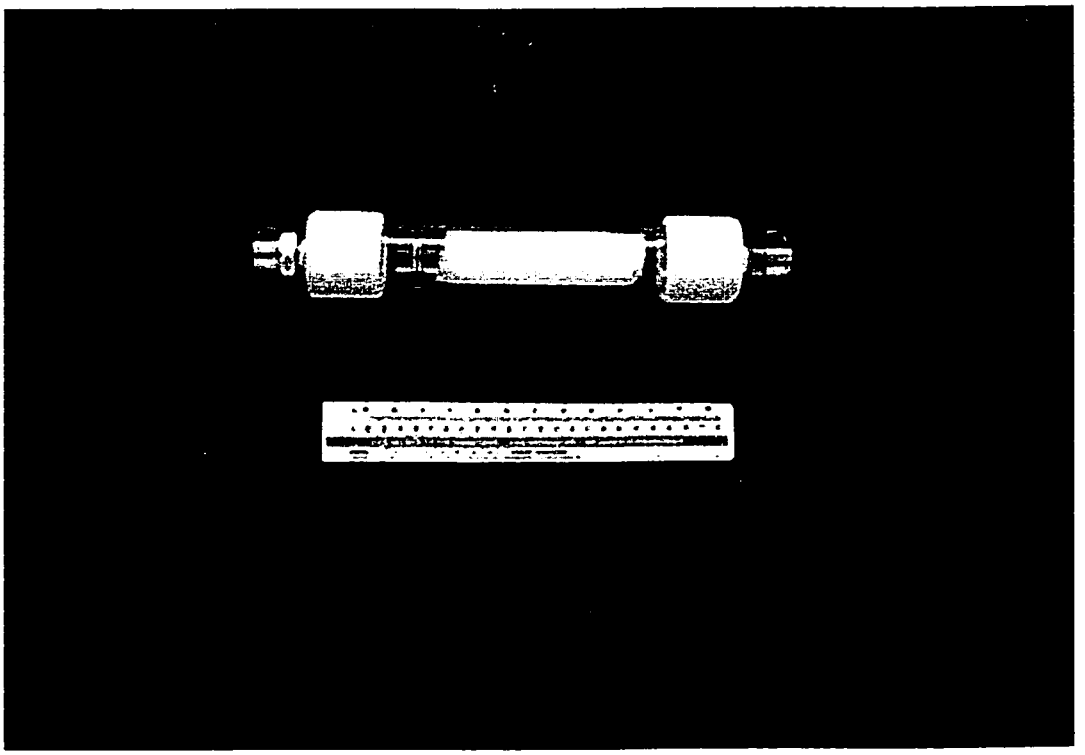


Plate 4.2 Polyurethane Foam Inserts in Glass Holder

4.1.3 Smoke Generation and Sample Collection

The first step was to obtain source signatures of four types of commonly burned wood indigenous to Northern Alberta, birch, poplar, pine, and spruce. These were burned outdoors in a domestic wood stove with no restriction to the air supply. Firewood was purchased from commercial sources and all of the wood had been dried for at least 1 year. As the supply of spruce cordwood was scarce, dimensional spruce lumber (2x4's) was used in Phase II. The smoke generation and collection train is illustrated in Figure 4.2.

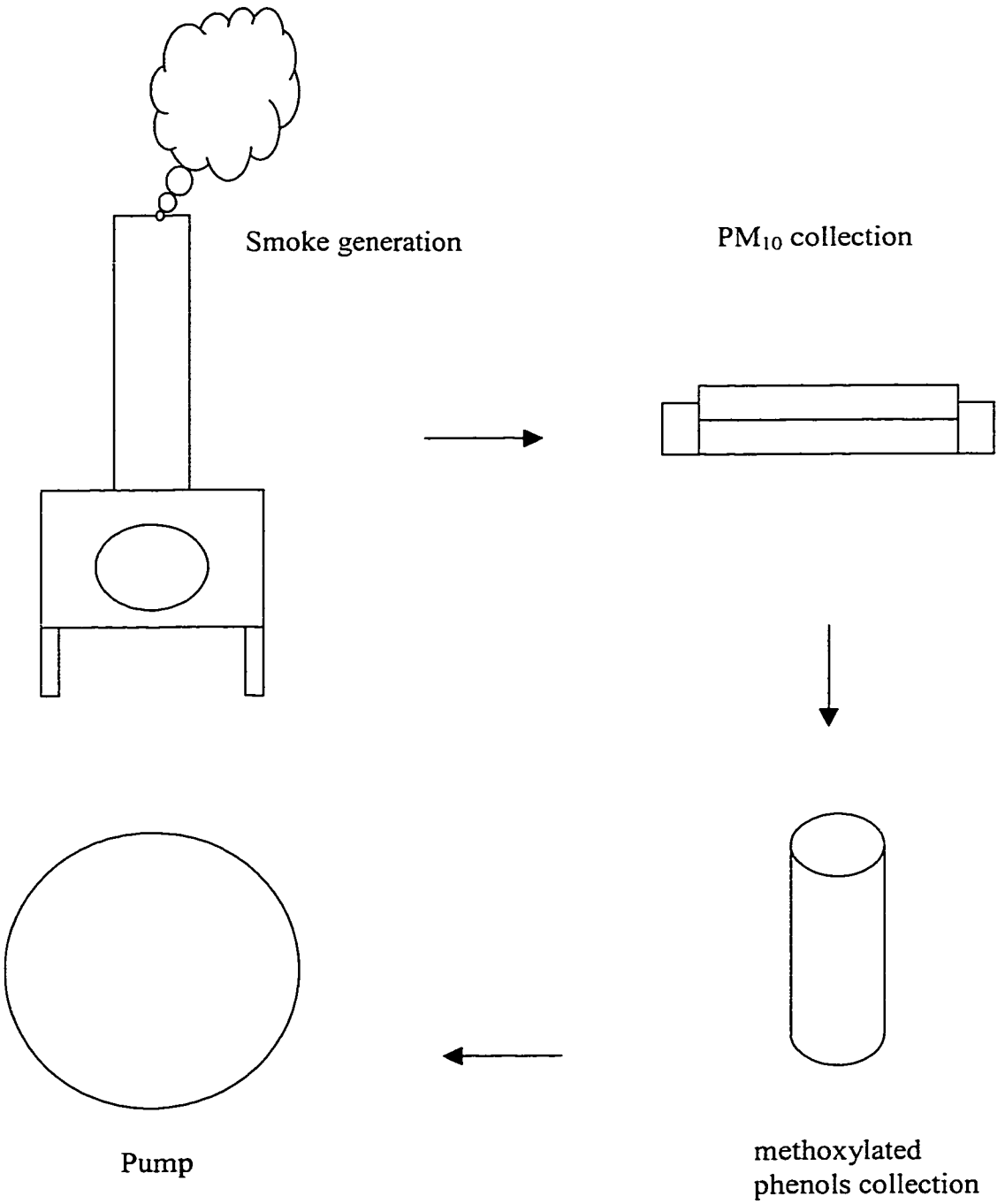


Figure 4.2 Smoke generation and collection train

4.1.3.1 Collection Protocol

- Prior to the collection process, careful observation was made to ensure the sampling area was not impacted by wood smoke from any nearby sources.
- The loading of the Marple PM_{10} impactor and the PUF holder was performed indoors away from outdoor areas possibly impacted by smoke.
- The interior of the Marple impactor cover was cleaned with "Kimwipes" to remove any particulate matter prior to the loading of the cellulose support filter and the quartz filter. Before loading, the quartz filter was also visually checked to ensure it was intact and free of foreign matter. The impactor ring was then oiled, with light mineral oil to minimize particle bounce. The two halves of the impactor were bolted together with screws.
- Full PUF filter and half PUF (in Phase I) were then loaded into the glass holder to the front and back positions respectively using a pair of clean stainless steel forceps. Connector caps were then attached securely at each end of the holder. The contact between the PUF filter and the internal surface of the glass holder was checked visually to ensure a snug fit to prevent channelling.
- The PM_{10} impactor and the PUF holder were then taken outside and the sampling train was assembled accordingly (Plate 4.2).
- The air-pump flow rate was verified with a flow calibrator (Gilibrator-2, Gilian Instrument Corp., NJ). The flow meter was connected to the Marple impactor with a coupler. The flow rate was then adjusted as close as possible to 10 LPM (STP) after taking the current barometric pressure and ambient temperature into account. The flow rate was verified with the flow meter before and after each sampling run. In the event of differences, the average flow rate was used for calculation purposes.
- The impactor was placed at a position within the smoke plume (Plate 4.3).
- Sampling began when the combustion chamber temperature reached near 375 ^{o}C. The temperature was checked utilizing a Raytek laser thermometer.
- After 15-minute sampling, the impactor and the PUF holder were removed from the assembly. In a clean indoor environment, the filters were unloaded.

The quartz filter was placed in a cassette and the PUF filters in hexane- and acetone- washed 40-mL glass vials. PUF filters were immediately stored in a freezer until transportation to the laboratory. The sub-zero temperature was maintained with insulated coolers during transportation. Samples were then stored in a laboratory freezer set at –50 °C until extracted for analysis.

- The impactor and the PUF holder were re-loaded as described above for the next sampling run.

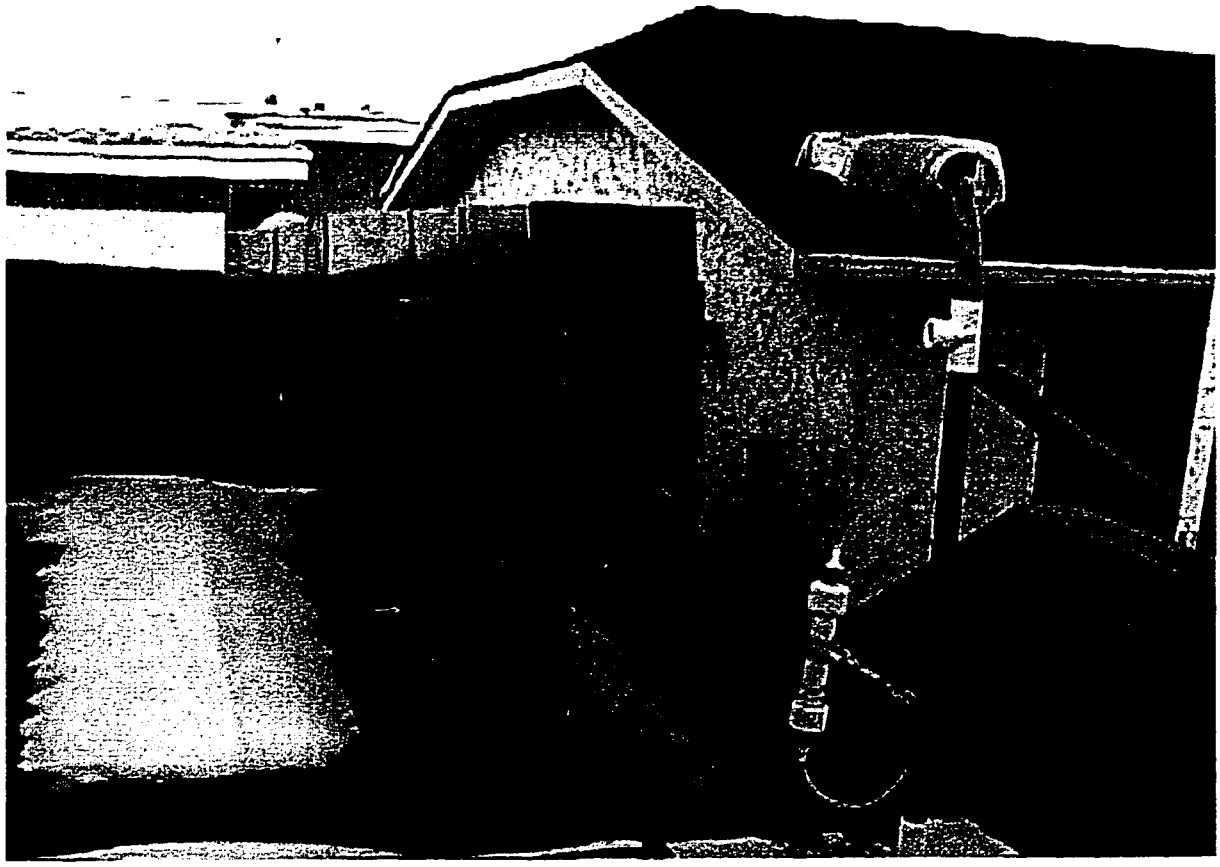


Plate 4.3 Monitoring Equipment in relation to Diversion Duct

4.1.3.2 Sampling (Phase I, April, 1997)

Firewood was combusted in a free-standing domestic wood-burning stove placed outdoors. Since combustion temperature was a significant factor influencing the type and quantity of combustion by-products, a relatively constant target combustion temperature was maintained by leaving the stove door and damper in open positions, which provided an unobstructed air supply. The combustion chamber temperature was always maintained at a minimum of 375 ^{o}C, the lowest temperature for wood residue burners permitted by Alberta Environmental Protection (AEP). The vertical section of the chimney was approximately 6 feet high and was connected to a slanted 10-foot section. This slanted section directed the smoke to the sampling equipment placed at an appropriate elevated location. The diversion section was constructed with non-insulated galvanized steel so as to facilitate a more rapid cooling effect.

Samples were collected in the middle of the smoke plume off the end of the diverter. The impactor was placed in the plume at a point slightly above the ambient air temperature. The distance was usually approximately 3 feet from the opening of the diversion duct, and it was adjusted whenever necessary depending on air flow and wind direction. Firewood was added whenever needed, and the sampling of particulate matter and methoxylated phenols from each wood species continued throughout all stages of burning. Adding of fuel wood in stages and continuous sampling were necessary in order to create conditions representative of emissions for various stages of a realistic, complete burn cycle.

Procedures were in place to minimize the influence from the previous wood type. Before changing to a new wood type, ash and remaining un-burned wood were removed from the combustion chamber as much as possible, and the new fire was allowed to burn for 15 minutes prior to any emission collection.

4.1.3.3 Sampling (Phase II, February, 1998)

The general protocol remained the same as in Phase I with some improvements to the sampling train. The slant diversion section was increased

from 10 feet to 19 feet in Phase II to allow better cooling, mixing, and longer time for chemical reactions. During Phase I, the high moisture content in the smoke had caused quartz filters to saturate and making them extremely difficult to recover without loss of filter material. Because of this experience, the emitted smoke in the second run was diluted to achieve an approximate 6:1 dilution factor with clean ambient air (Stevens, 1985), using a domestic electric fan. However, the dilution factor fluctuated depending on wind direction, velocity, burn-rate and quantity of wood being burned. In general, the 6:1 dilution factor was roughly maintained. This added dilution procedure simulated plume formation, but unfortunately, the introduction of cool air did not prevent the quartz filters from becoming saturated with moisture. The relative humidity was still near 100% due to the rapid cooling of the smoke plume by the cold ambient air.

4.2 Smoke Dilution

To facilitate the introduction of extra air, an opening was cut at the end of the diversion duct. Dilution was achieved by placing a 12-inch domestic fan at the end of the duct (Plate 4.4).

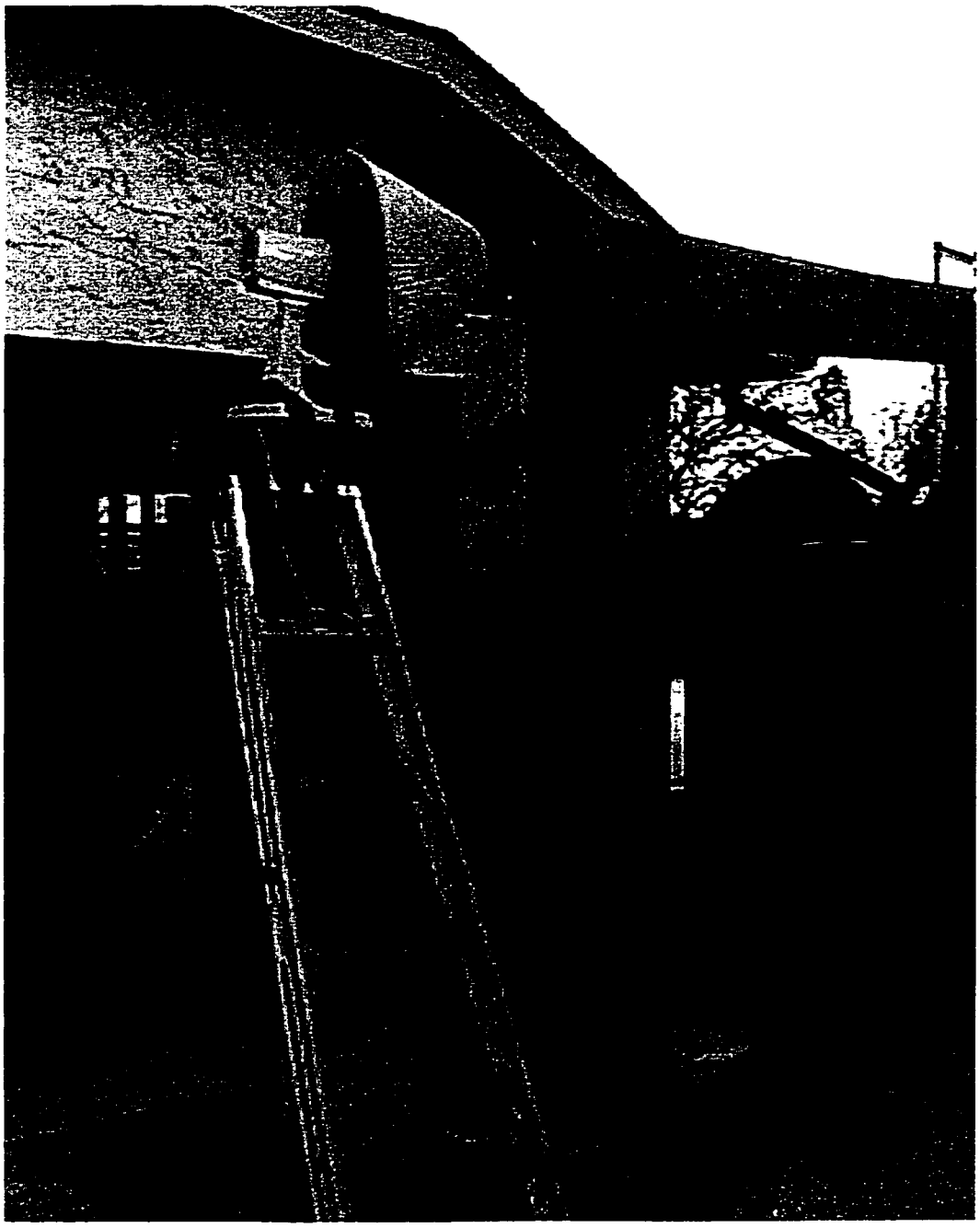


Plate 4.4 Dilution Fan at End of Diversion Duct

The initial flow-rate at the outlet without the extra supply of clean ambient air was initially recorded with a velometer. Then clean air was injected through the opening of the diversion duct. Since the surface area of the outlet remained constant, the 6:1 dilution factor was determined by adjusting the final flow-rate to 7x the initial one.

As a 12-inch domestic fan was used to supply the additional fresh ambient air to achieve the targeted 6:1 dilution factor, it was a concern that the electrical fan motor might generate PM_{10} and affect the particulate matter concentration of the wood smoke. A test was therefore performed to evaluate this possibility. On January 28, 1998, the air plume generated by the fan was monitored with a real time PM_{10} monitor, TEOM Series 1400a (Rupprecht and Patashnick, Co., Inc.) in the Environmental Engineering Laboratory at the University of Alberta. Prior to the testing, the TEOM monitor had been warmed up over night, and the fan had also been turned on for 30 minutes. PM_{10} concentration from the plume of air generated by the fan was monitored for 1 hour. The laboratory was vacated during the monitoring period to avoid the influence of human activities. Six readings taken 10 minutes apart were compared with readings of background PM_{10} mass concentrations taken just prior to the testing of the fan. The t-test on the two sets of readings indicates there was no difference. The test outcome is described in the "Results" section.

4.3 Positive Controls

Wood combustion and diesel fuels are major sources of particulate carbon in ambient air (Mulhbaier and Williams, 1982; Dasch and Cadle, 1989; Brown et al., 1989; Dod et al., 1989; Hansen and Rosen, 1990; Burtscher, 1992). In order to verify that wood combustion is the sole source of guaiacol and derivatives, motor vehicle emissions, both gasoline and diesel, were collected with the sampler and analyzed (Plate 4.5). For consistency, the sampling train was arranged in exactly the same manner as the wood-smoke source signature collection. A Marple impactor with a quartz filter was fitted to the train. Gravimetric analysis was not performed on the quartz filter because the mass

emission rate was not required. Results are provided in section 5.7.

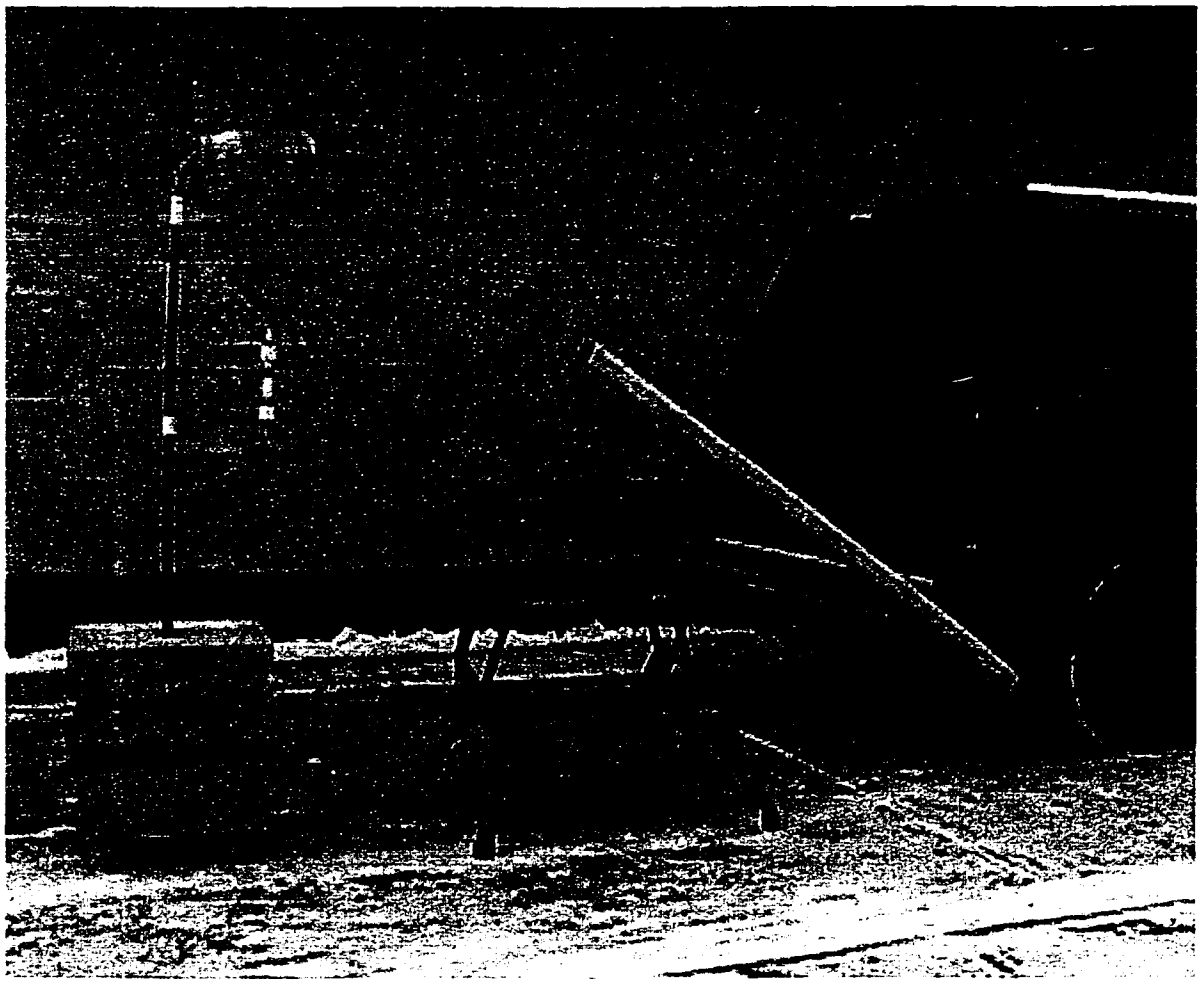


Plate 4.5 Collection of Fossil Fuel Exhaust

4.4 Laboratory Procedures and Analyses

Gravimetric analysis of the inhalable particulate matter and the determination of carbon content were performed at the Air Pollution Laboratory of the Alberta Research Council, Vegreville, Alberta. All GC/MS procedures were performed at the Environmental Health Sciences Laboratory, University of

Alberta. Acetone (Optima) and hexane (Optima) were the 2 major solvents used in preparation, extraction, and dilution procedures. Both solvents were HPLC grade and were supplied by Fisher Scientific.

4.4.1 Gravimetric Analysis

This procedure was performed by the Alberta Research Council staff. It involved the equilibration of quartz filters at constant temperature and humidity, and the gravimetric determination of the mass of the collected particulate matter.

4.4.1.1 Visual Inspection and Conditioning of Filters

Prior to weighing of new quartz filters, the filters were inspected for damage by holding against a light source. Unacceptable filters were either discarded or used as "lab blanks". Each of the acceptable filters was placed in an individual 50-mm diameter pre-labelled petri dish using teflon-coated filter tweezers. The open petri dish together with a quartz filter were placed in a humidity controlled cabinet and was allowed to equilibrate under constant temperature and humidity for 24 hours. Prior to weighing, the dishes were placed inside a humidity-controlled weighing cabinet, opened and allowed to adjust to the 50% relative humidity for 24 hours with a datalogger/humidity controller (Campbell CR-21) at 22 °C. A record of humidity and temperature was made for both pre-conditioning and subsequent filter weighing time using computerized automatic data collection.

4.4.1.2 Pre-sampling Weighing

In order to determine the mass of the collected particulate matter, the original mass of the individual new quartz filter prior to collection must be accurately determined using an electronic microbalance (Cahn Model 30). Filter weighing was performed using a computerized automatic data collection program that controlled the balance weighing sequence, reading stabilization and data storage. After weighing, each filter was returned to the petri dish, sealed and was ready for sampling.

A control filter was weighed before and after each set of weighing process. The two readings should not differ by more than 0.005 mg. The calibration of the balance was also checked after every 25 weighings and at the end of each set of weighings. After all conditions were determined to have been met, the weight of the filters was then recorded. Each of the filters was placed in a petri dish, sealed, and stored in a horizontal position ready for sampling.

4.4.1.3. Post-sampling Weighing

Filters were returned to the laboratory after each experiment for post-sampling weighing. The weighing and equilibrating procedures were the same as the pre-sampling procedure as described above. The mass of the collected particulate matter was determined by noting the difference between the two weighings.

4.4.2 Total Carbon Determination

This procedure was also performed at the Alberta Research Council. The method is based on the thermal combustion with an elemental analyzer (LECO, Model CHNS-932) at 950 °C of the particulate matter in the presence of tungsten trioxide, which converted carbon components to carbon dioxide. Carbon oxides were measured in sequence in three infrared cells.

Procedure

- A small disc of known area was cut from the loaded quartz filter.
- The inner exposed portion of the filter disc was folded into quarters, rolled and placed into a tin cup which was then crimped and folded.
- Blank filter discs were prepared following the above steps.
- The analyzer was then calibrated using a certified standard, 3,5-dinitrobenzoic acid, followed by two blank filter papers.
- Factors for blank, calibration and weight were applied to the final, integrated signal, and results were automatically calculated and displayed in weight percent.

4.4.3. Preparation and Extraction of PUFs

Polyurethane foam sorbent has advantages such as easy handling, effectiveness for absorbing vapour phase organic compounds, and easy extraction. However, solvent extract blanks can contain high concentrations of organic contaminants (Guenther, 1987). To ensure that quality data were obtained, the PUF plugs were exhaustively extracted prior to the collection of samples.

4.4.3.1 Pre-sampling Preparation/cleaning

Prior to sampling, all PUFs were extracted to remove as much organic matter from the absorbent as possible. The PUFs were submersed in hexane in a beaker and sonicated for 30 minutes. Then the PUFs were squeezed with a spatula to remove hexane. The PUFs were again submersed in acetone and sonicated for 30 minutes. After squeezing out the acetone, the PUFs were placed in a beaker covered loosely with clean tinfoil and dried on a hot plate at a low setting. To accelerate the drying process, a small stream of clean nitrogen was introduced into the beaker. After drying, the clean PUFs were stored in wide-mouth glass jars fitted with teflon lids and were ready to use.

4.4.3.2 Extraction

After sampling, PUFs were extracted to recover guaiacols for GC/MS analysis. Prior to the first sonication:

1. A laboratory blank was made up with acetone, and 100 μL of 10 μg/mL guaiacols standards was added (preparation of the internal standard is described in the GC/MS section).
2. The blank and all PUFs were spiked with 100 μL of 10 μg/mL internal standards, 4'-bromoacetophenone and 5-chloro-1, 3-dimethylbenzene.

First Sonication

- Enough acetone was added to the 40-mL vials to just cover the PUFs.
- Vials were sonicated for 30 minutes in a water bath.
- After the first sonication, acetone was removed and collected in labelled

round-bottomed flasks.

Second Sonication

- The vials containing squeezed PUFs were again filled with acetone and then sonicated for 15 minutes.
- Acetone was again squeezed out and collected in corresponding round-bottomed flasks.

Reduction of Acetone Extract (to 1.0 mL)

- Using a rotary evaporator (Rotavapor R-444, Buchi, Switzerland) and a water bath (B-481, Bucchi, Switzerland), the acetone extract volume was reduced to approximately 1 mL. The evaporator was set at 556 mbar vacuum, and the water bath temperature was set at 40 °C.
- The volume-reduced extract was then transferred to calibrated test tubes; round-bottomed flasks used in the rotary evaporation were each rinsed twice with acetone. The wash was transferred to corresponding calibrated test tubes.
- The extracts in calibrated test tubes were concentrated to 1 mL with clean nitrogen.
- the final 1-mL extracts were transferred to 2-mL GC-MS crimp vials using micro-pipets and were ready for analysis.

4.4.4 GC/MS

Quantification of each species was based on the integrated area of its molecular ion compared to that of the internal standards, 4'-bromoacetophenone, and 5-chloro-1, 3-dimethoxybenzene. For quantitative anlaysis, the MSD was operated in *Selected Ion Monitoring* mode (SIM). In this mode, only particular ions of interest are monitored, which results in greater specificity and enhanced sensitivity.

4.4.4.1 Calibration

To prepare the analytical standard solution, 50 mg of guaiacol and studied derivatives were weighed and placed in a 50-mL volumetric flask. The volumetric

flask was then filled with acetone to the 50-mL mark. The concentration of the guaiacol analytical standard solution was 1000 µg/mL. In both Phases, calibration was based on three-point standard curves generated using authentic standards for each individual species at 10x, 100x and 1000x dilution (100 µg/mL, 10 µg/mL, and 1 µg/mL respectively).

An estimate of method detection limit (MDL) was based on 3x background noise. Method detection limits for methoxylated phenol tracers used in this study are listed in Table4.1.

Table 4.1 Methoxylated phenol tracers dectection limits

Methoxylated Phenol Tracers	Method Detection Limits (µg/ml)
Guaiacol	0.03
4-methylguaiacol	0.2
4-ethylguaiacol	0.009
Eugenol	0.05
Vanillin	0.05
Isoeugenol	Not determined
Acetovanillone	0.02

4.4.4.2 Analysis

Phase I GC analyses were performed using a Hewlett-Packard Model 5890 Series II gas chromatograph, and MS analyses were performed using a Hewlett-Packard 5970 Series Mass Selective Detector (MSD). Injections (1 µL) were in the splitless mode into a 30-m DB-5 (250 µm i.d., 0.25 µm film thickness). The GC oven temperature program was maintained at 70 °C for 1 minute followed by a temperature ramp at 8 °C /minute to 260 °C. All species were identified on the basis of comparisons of their mass spectra and retention indices compared with that of authentic standards. Additionally, authentic standards were used for all of the derivatives of guaiacol. For quantitative analyses, the MSD was operated in selected ion monitoring mode (SIM). In this mode, only particular ions of interest are monitored, which results in greater specificity and enhanced sensitivity.

Phase II In Phase II, a Varian Saturn 2000 GC/MS instrument was used to

analyze the PUF extracts. The Saturn 2000 mass spectrometer is a bench-top *ion trap* system. Because there is no separate ion source, ions are not lost in the travel space between the ionization chamber and the analyzer. Improved from the *quadrupole*, the *ion trap* has better resolution, a faster scan rate, no separate ion source, and a better efficiency of detection. As a result of the faster scan rate, higher sensitivity is achievable because smaller peaks can still be measured accurately. For guaiacols quantification, the instrument was operated in selected ion storage (SIS) mode.

5. RESULTS

5.1 Loss of Filter Material

In Phase I, five smoke samples were obtained from each wood type. However, due to laboratory errors, and breakage of the particulate filter material during the unloading process after sampling, few samples were suitable for quantitative analysis. Therefore, an additional phase (Phase II) was necessary and was eventually carried out in early 1998. The collection methodology was improved in the second phase - ambient air was introduced to the smoke collection duct to dilute the smoke approximately six times prior to collection (see section 4.2.3). It was hoped that the smoke humidity would be lowered with this additional dilution, resulting in less moisture saturation and condensation on the quartz filters, and facilitating easier filter unloading and eliminating breakage of filter material. Unfortunately, while the absolute moisture content in the smoke plume decreased, the relative humidity of the smoke remained at near 100% due to the rapid cooling of the smoke plume as it was leaving the collection duct. Quartz filters for PM_{10} collection remained saturated with moisture, and consequently the loss of filter material due to breakage during removal was not prevented. The effect of filter material loss was significant and was easily observed in the "negative" weights of PM_{10} as reported by the Alberta Research Council (ARC) (Table 5.1). Consequently, the PM_{10} gravimetric data generated in Phase II were not used for analysis due to a lack of confidence. Fortunately, as described in the laboratory analysis section, ARC had determined the total carbon content on the filter by extrapolating data obtained from a sample disc cut from the filter. The loss of filter material, therefore, did not preclude the estimate of carbon content. The carbon content obtained with this methodology was reliable and was suitable for quantitative analysis. However, some PM_{10} filters had uneven collection patterns due to break-through conditions. The root cause of this condition was due to the absorbent nature of quartz material. The edges of some quartz filters were noted to have curled up slightly when delivered by the manufacturer, presumably due to previous exposures to moisture. A decrease in the actual diameter of the filter resulted in a poor seal when loaded onto the

impactor. Previous studies have found that carbon makes up more than 80% of the overall smoke particulate content (Cooper and Malek 1982; Kleinman et al., 1980; Stevens, 1985). Assuming that PM_{10} samples collected in Phase II also had a carbon content at 80%, a quick quality control check has been performed by comparing the actual PM_{10} weight on the filters as reported by ARC with the expected PM content as calculated. Filters with no loss of filter material should have similar or matching reported and expected weights of PM. When reported PM_{10} content is less than the expected weight, it indicates some degree of filter material loss due to breakage. Results have revealed that most filters have some degree of material loss (Table 5.1).

Table 5.1 Comparison between Laboratory Reported Weight and Theoretical Weight of PM10 (Phase II)

Sample ID	Average Carbon on filter (mg)	Theoretical weight of PM_{10} (mg)	Actual weight of PM10 on filter (mg)	Filter Material Loss (likely)
Birch 1	0.09	0.11	0.17	**No**
Birch 2	0.26	0.33	0.30	Yes
Birch 3	0.13	0.16	0.18	Yes
Birch 4	0.47	0.59	-1.85	Yes
Birch 5	0.30	0.38	0.12	Yes
Birch 6	0.17	0.22	0.17	Yes
Birch 7	1.10	1.38	1.49	Yes
Birch 8	0.84	1.05	1.07	**No**
Birch 9	0.26	0.33	0.19	Yes
Birch 10	0.30	0.37	-0.25	Yes
Poplar 1	0.45	0.56	-0.61	Yes
Poplar 2	0.41	0.51	0.05	Yes
Poplar 3	0.18	0.22	-0.90	Yes
Poplar 4	0.13	0.16	0.03	Yes
Poplar 5	0.23	0.29	-0.20	Yes
Poplar 6	0.14	0.18	-1.27	Yes
Poplar 7	0.23	0.29	-1.09	Yes
Poplar 8	1.55	1.94	1.41	Yes
Poplar 9	1.01	1.26	0.43	Yes
Poplar 10	1.36	1.70	0.15	Yes
Pine 1	2.91	3.64	4.35	**No**
Pine 2	2.05	2.57	2.61	**No**
Pine 3	0.29	0.36	0.22	Yes
Pine 4	0.44	0.55	0.08	Yes
Pine 5	0.53	0.67	0.44	Yes
Pine 6	0.50	0.62	0.09	Yes
Pine 7	0.39	0,49	-0.49	Yes
Pine 8	0.39	0.49	0.17	Yes
Pine 9	0.92	1.15	1.30	No
Pine 10	0.39	0.49	0.46	Yes
Spruce 1	0.29	2.86	3.33	**No**
Spruce 2	1.31	1.64	1.89	**No**
Spruce 3	0.90	1.12	1.10	Yes
Spruce 4	0.63	0.79	0.65	Yes
Spruce 5	1.14	1.42	0.67	Yes
Spruce 6	2.24	2.79	2.84	**No**
Spruce 7	3.66	4.58	5.42	**No**
Spruce 8	0.56	0.70	0.15	Yes
Spruce 9	0.52	0.56	0.39	Yes
Spruce 10	0.39	0.49	-0.43	Yes

In all cases, PM_{10} gravimetric data and carbon content data from uneven collections were not used for smoke profile determination. On the other hand, methoxylated phenol data obtained from all PUF filters were independent of the quartz filters data (from small cut discs) and remained suitable for qualitative analyses of methoxylated phenols.

In addition to wood smoke chemical quantitative profiles, inter- and intra-specific smoke sample patterns were also compared. Results are presented under **Phase I** and **Phase II** headings. The graphs have been generated based on normalized data (guaiacol concentrations normalized to 1.0) and do not reflect absolute quantities. Through comparison of the pattern, insight into factors affecting the smoke profile was sought.

5.2 Phase I

5.2.1 Birch

The methoxylated phenols pattern in birch smoke is depicted graphically in Figure 5.1. With the exception of Birch 1, guaiacol was the most prominent species. Sample Birch 3 also showed some slight variation in its pattern in that vanillin was present in a significant quantity. 4-methylguaiacol and 4-ethylguaiacol were present in all samples in quantities much less than that of guaiacol. Other guaiacol derivatives species were not detected.

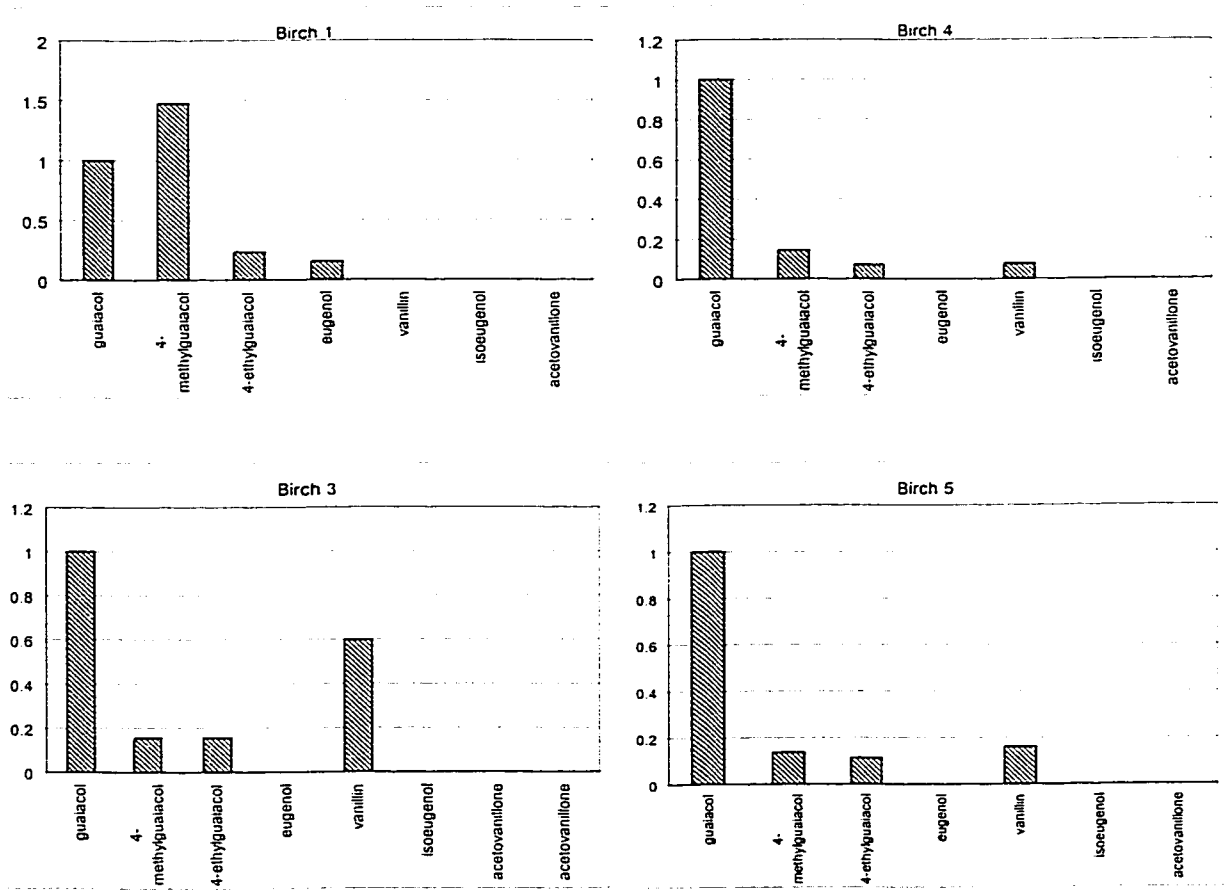


Figure 5.1 Birch smoke profile (Phase I), based on blank-subtracted data, normalized to guaiacol

5.2.2. Poplar

The presence of methoxylated phenols in poplar smoke is depicted graphically in Figure 5.2. Similar to birch, guaiacol was the most prominent species. 4-methylguaiacol and 4-ethylguaiacol were both present at about one-fifth of the quantity of guaiacol. Eugenol and vanillin were also present while isoeugenol and acetovanillone were not detected. Overall the observed pattern for poplar were relatively consistent.

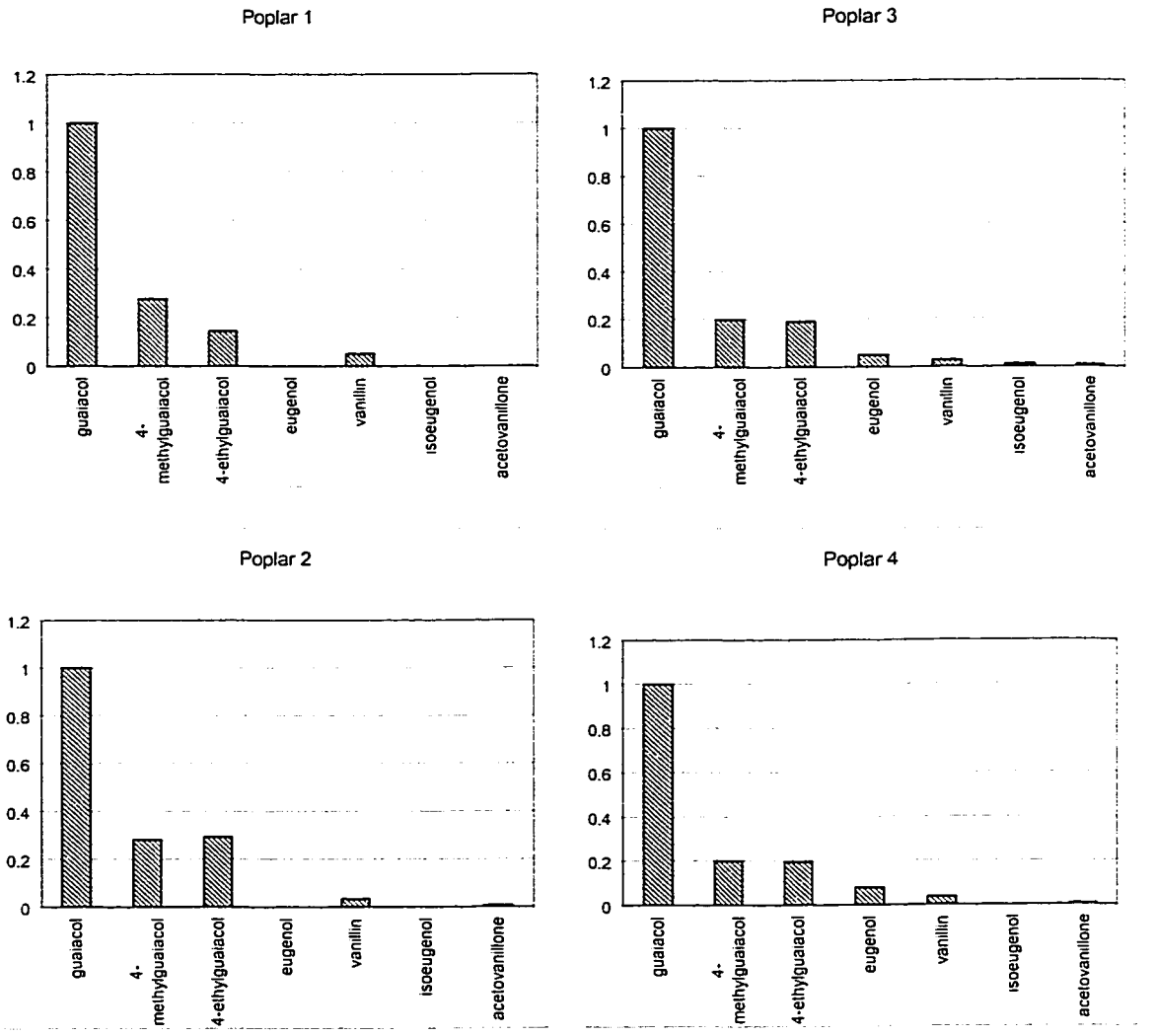


Figure 5.2 Poplar smoke pattern (Phase I), based on blank-subtracted data, normalized to guaiacol

5.2.3 Pine

The presence of methoxylated phenols in pine smoke are depicted graphically in Figure 5.3. Again, guaiacol was the major species while the relative quantities of 4-methylguaiacol and 4-ethylguaiacol varied between samples. In one sample (Pine 2), 4-ethylguaiacol was not detected. In the same sample, vanillin was the second most dominant species after guaiacol. In another sample (Pine 5), while 4-ethylguaiacol was detected, 4-methylguaiacol was not. Acetovanillone was detected in two samples (Pine 2 and Pine 4). Overall these patterns were not very consistent except for the dominance of guaiacol.

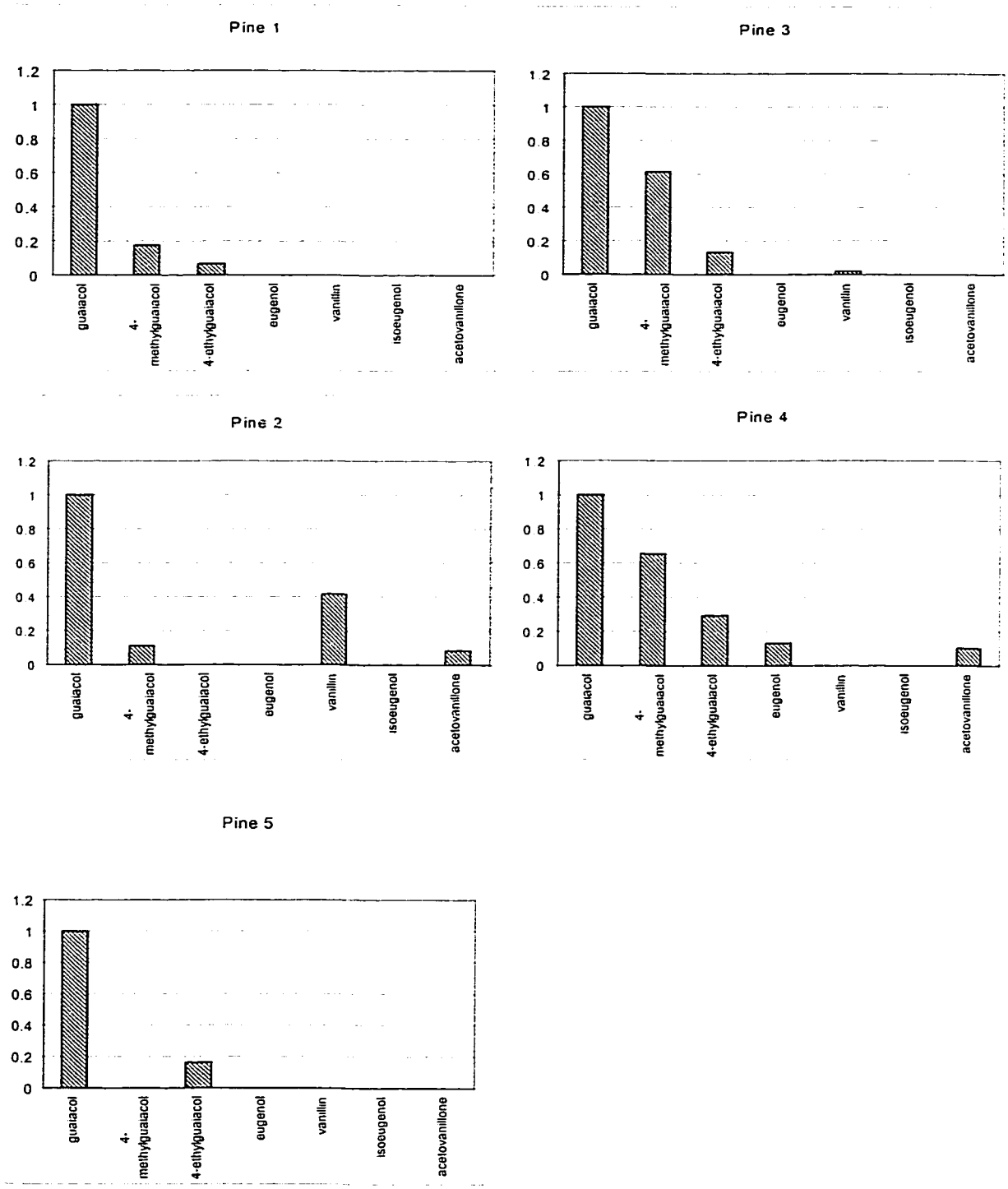


Figure 5.3 Pine smoke pattern (Phase I), based on blank-subtracted data, normalized to guaiacol

5.2.4 Spruce

The presence of methoxylated phenols in spruce smoke is depicted graphically in Figure. 5.4. Guaiacol was the major species in all samples, with the exception of spruce 1. Notably vanillin was a major species, as similar to Pine 2, surpassing 4-methylguaiacol and 4-ethylguaiacol in three of the four samples. Acetovanillone was also detected in small quantities in two samples, as it was in two of the pine smoke samples.

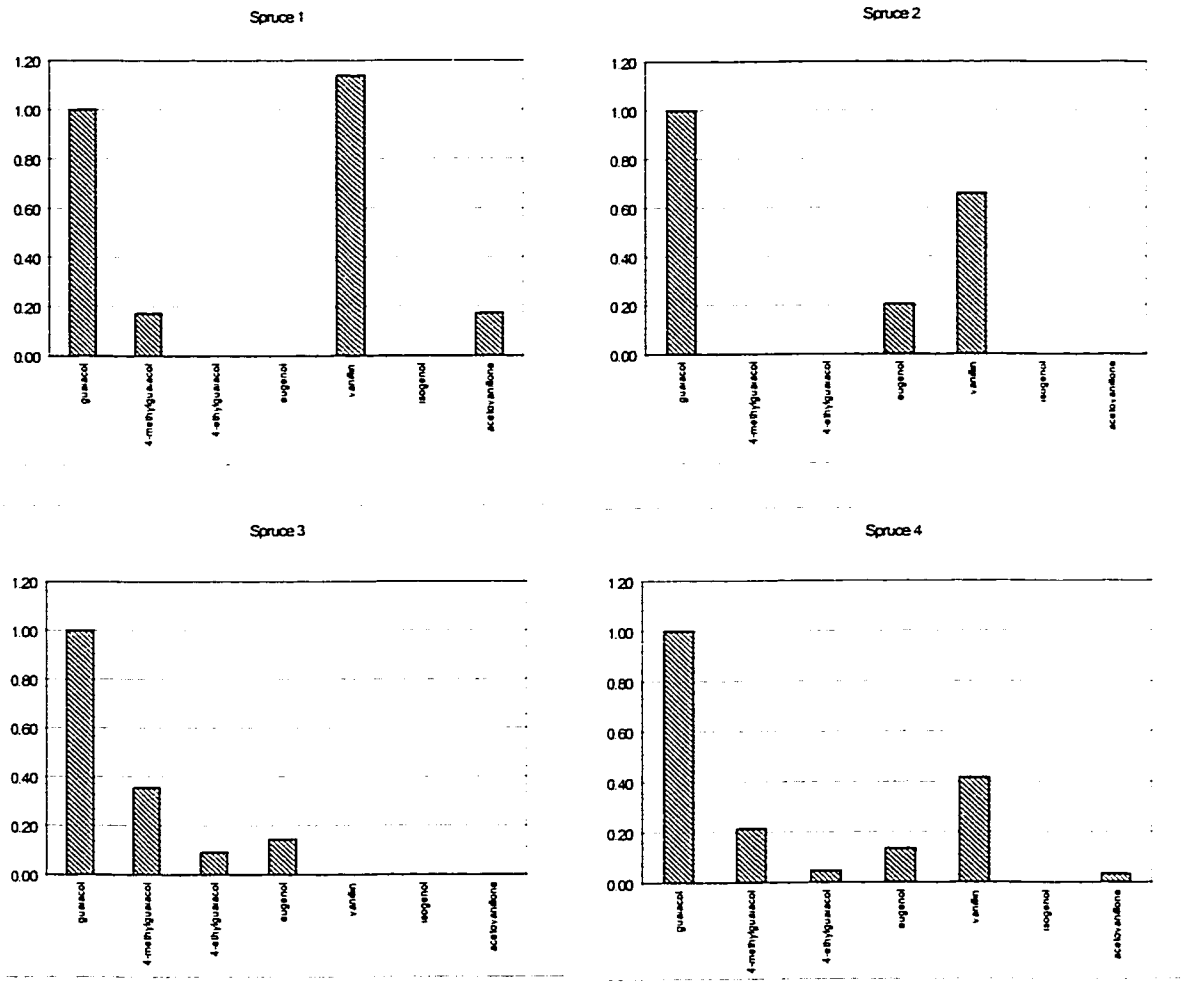


Figure 5.4 Spruce smoke profile (Phase I), based on blank-subtracted data, normalized to guaiacol

5.3 Phase II

Similar to Phase I, all wood species were burned under "hot burning" conditions with no restriction in air supply. Bearing in mind that the firewood was from different batches with different moisture contents, the combustion by-product chemistry could have been different from those of Phase I. Unlike Phase I, the wood-smoke was diluted approximately six times with ambient air prior to sampling. Moreover, the length of the diversion chimney was also nearly doubled. The dilution, as well as the increase in the retention time by lengthening the chimney, were aimed at better simulating ambient conditions and allowing a longer reaction time. These differences could collectively influence the relative patterns and account for some of the observed differences between Phase I and Phase II smoke profiles of the same wood types.

Furthermore, a new GC-MS instrument was used in Phase II to analyze the PUF extracts. MS analyses were performed using a Varian Saturn GC-MS. The computer software was programmed to show only the peaks of targeted compounds with specified mass. A sample chromatogram is shown in Figure 5.5.

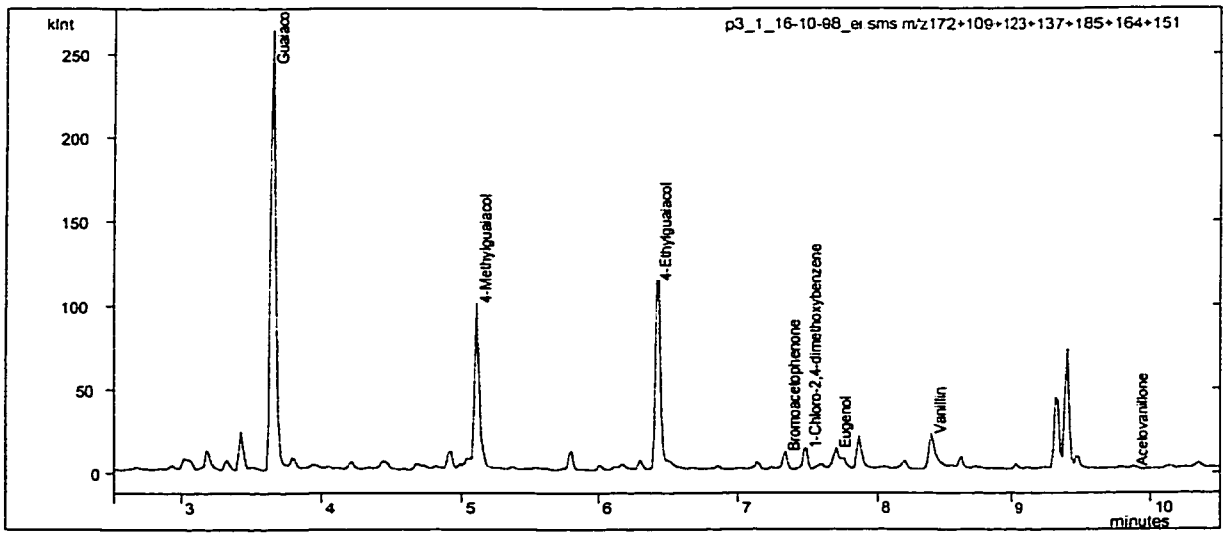


Figure 5.5 Sample MS chromatogram from Phase II (Poplar 3)
(chromatogram shown is a raw chromatogram and background has not been subtracted. Certain peaks, e.g. vanillin and eugenol, are shown here but are not quantified after background subtraction.)

Samples collected in Phase II are depicted graphically in Figures 5.6, 5.7, 5.8 and 5.9. Smoke profiles of birch, poplar and pine were very similar within each wood type. As in Phase I, spruce samples in Phase II differed from the other 3 types of wood smokes with the noticeable presence of some minor guaiacol species, but major contributions from vanillin were not observed in Phase II.

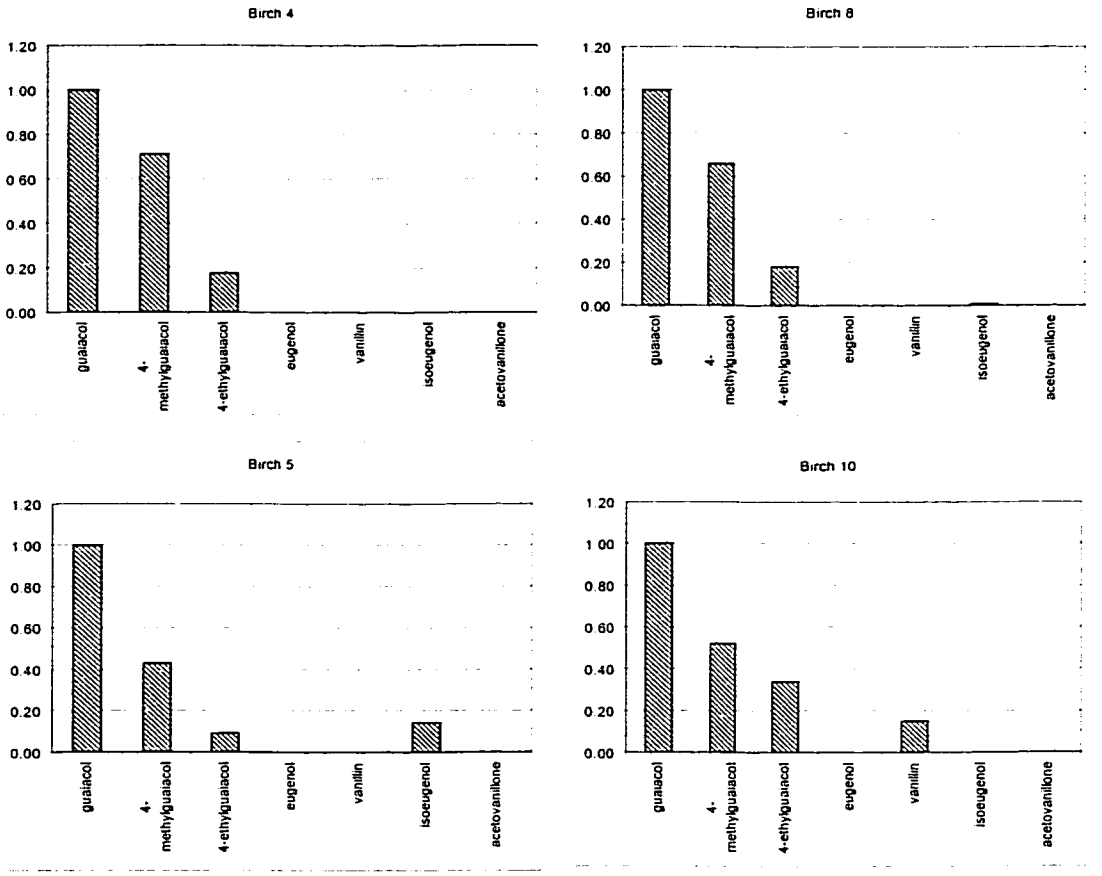


Figure 5.6 Birch smoke pattern (Phase II), based on blank-subtracted data, normalized to guaiacol

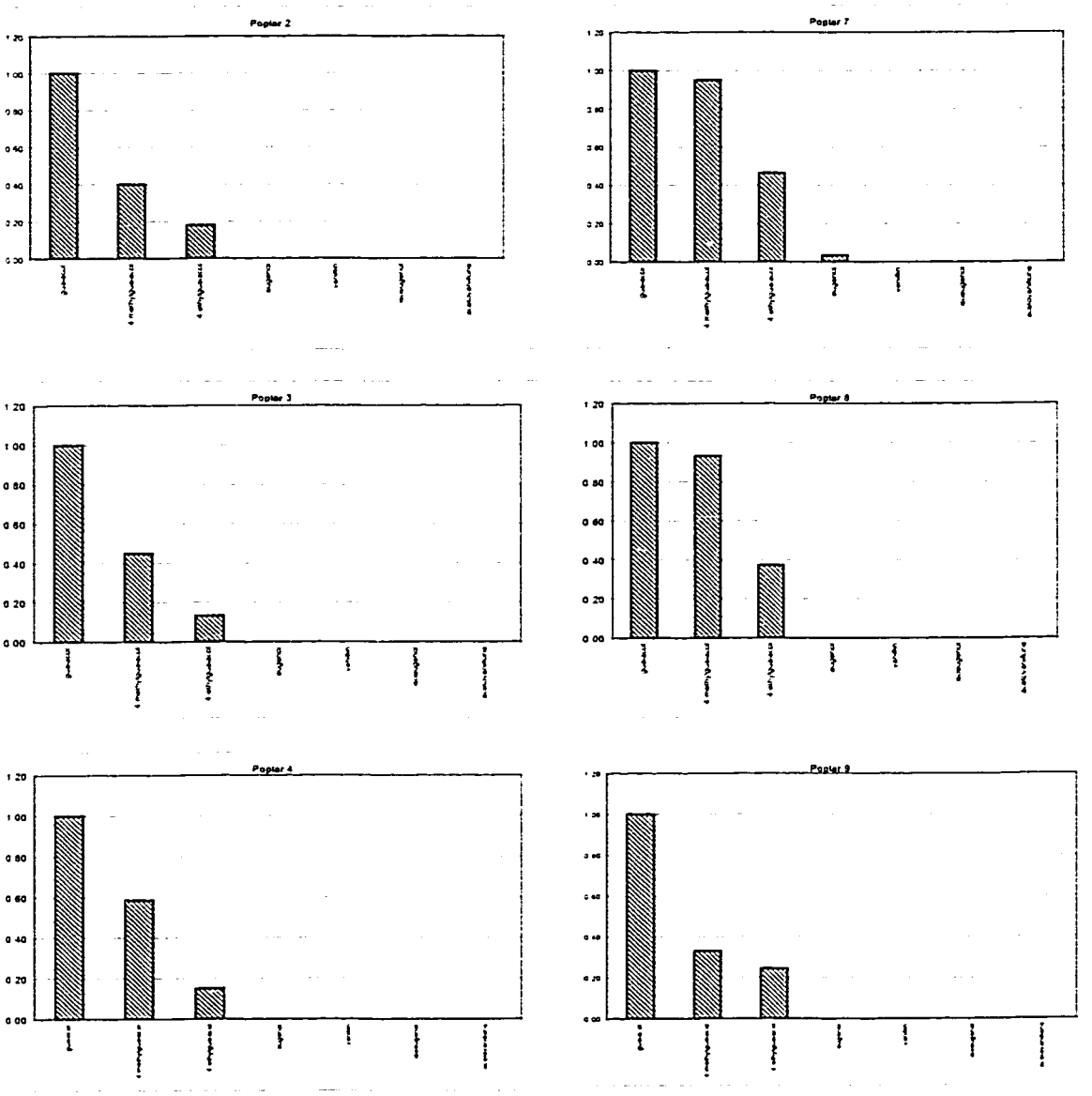


Figure 5.7 Poplar smoke pattern (Phase II), based on blank-subtracted data, normalized to guaiacol

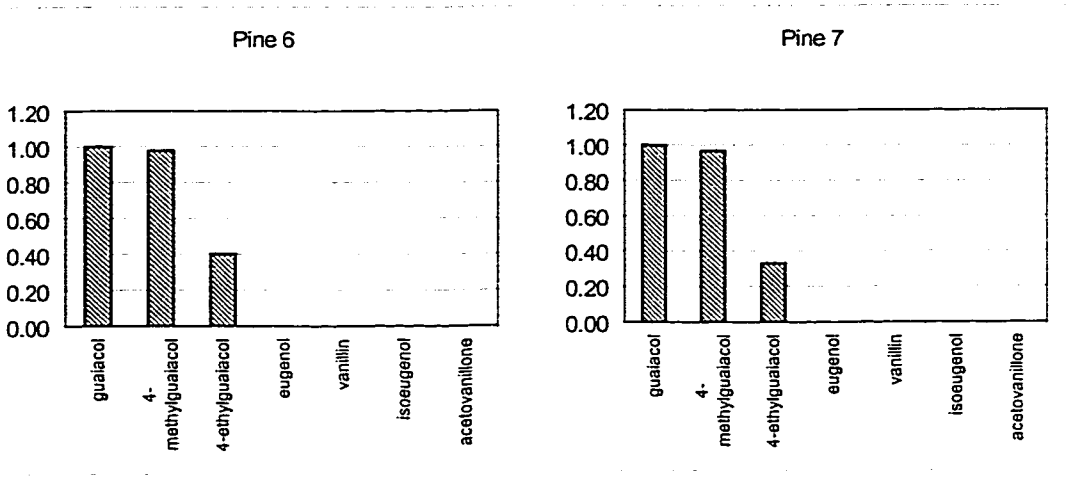


Figure 5.8 Pine smoke pattern (Phase II), based on blank-subtracted data, normalized to guaiacol (Smoke patterns of remaining pine samples are not plotted due to experimental or analytical factors, see Table A2).

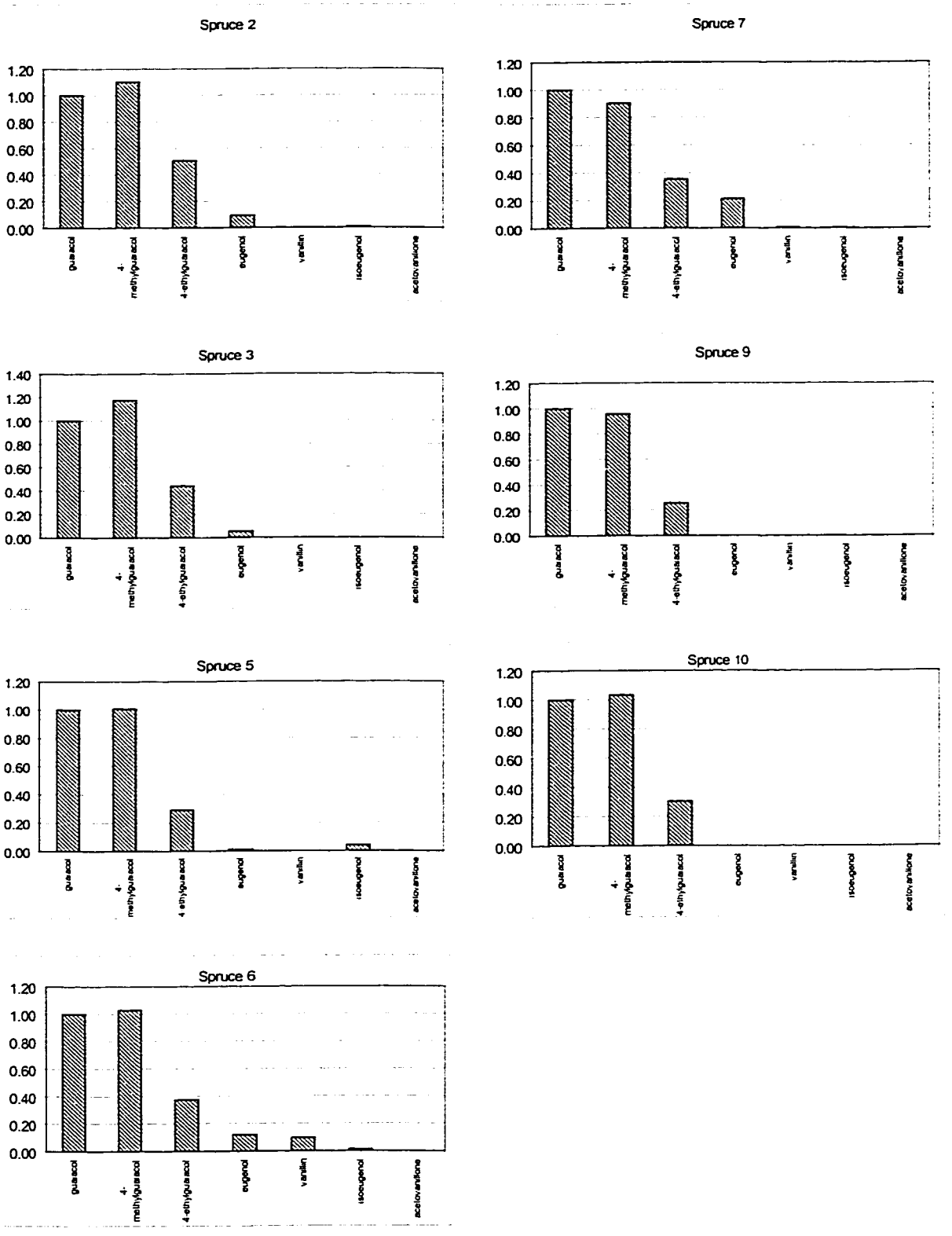


Figure 5.9 Spruce smoke pattern (Phase II), based on blank-subtracted data, normalized to guaiacol

5.4 Comparison between Phase I and Phase II

Figure 5.10 illustrates the graphical comparison of Phase I and Phase II composite (mean) smoke profiles. This comparison shows little similarity between results obtained in Phase I and Phase II. However, it was clear from looking at the individual samples that Phase II samples were much more consistent in the patterns observed. Given this consistency and improvements introduced to the sampling and analysis methods, the results are considered more reliable. The comparison also shows variability in the contents of vanillin in some of the samples.

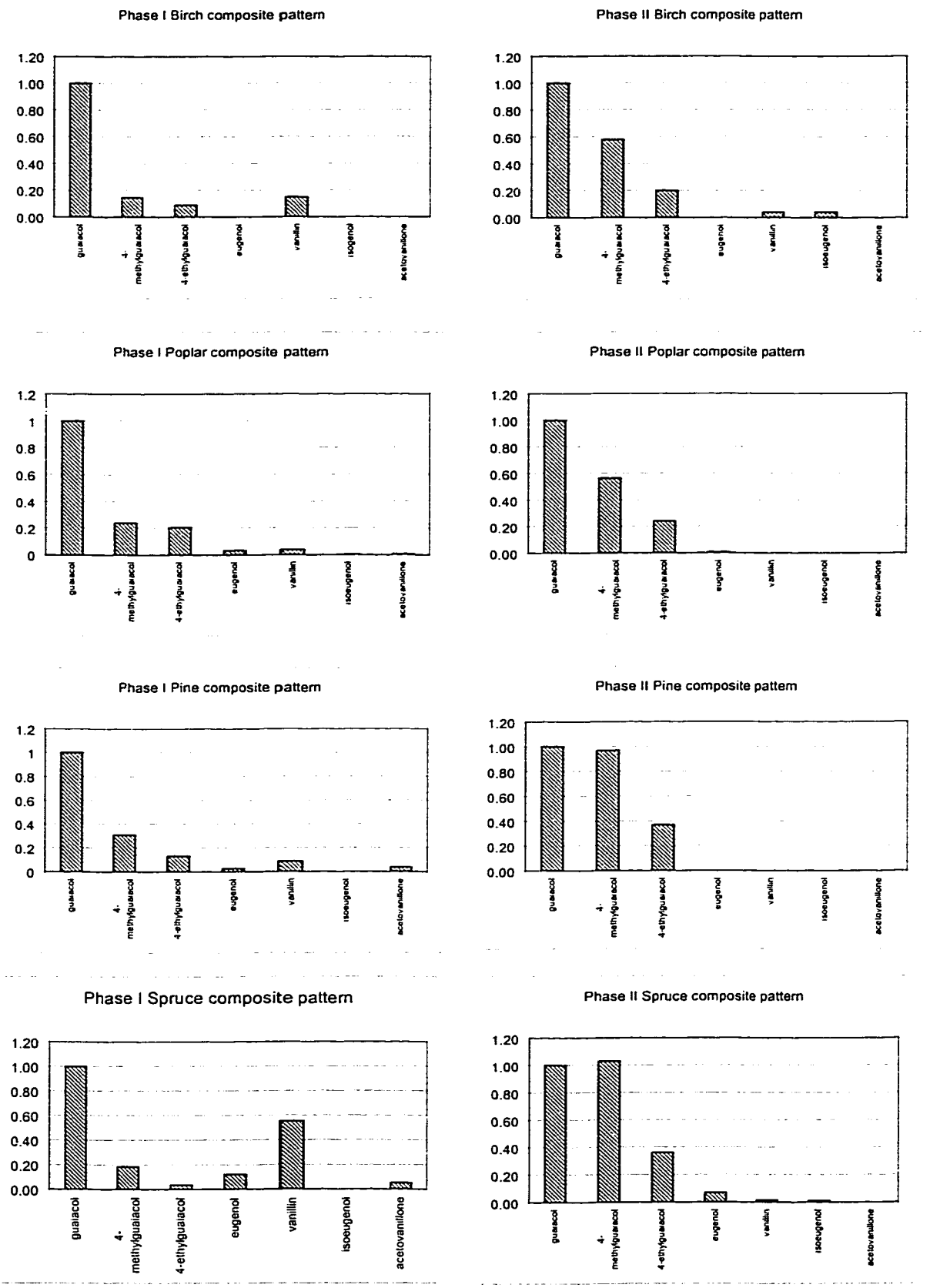


Figure 5.10 Comparison of composite smoke sample profiles from Phases I and II

5.5 Fan Influence

In Phase II, air stream from an electrical fan diluted the smoke plume volume by approximately six times in an attempt to decrease the smoke moisture content and hence to minimize saturation and loss of quartz filter material. However, there was concern that electrical motors could produce PM_{10}. Two sets of airborne PM_{10} concentrations were recorded with and without the influence of the electrical fan used to provide the 6:1 dilution as described in section 4.2. The numbers were analyzed statistically to calculate the variance and hence to determine the influence of the fan on PM_{10} concentrations (Table 5.2). The two sets of numbers were virtually identical. A t-test was performed on the two sets of numbers. The test statistic (t-value) (–0.1210) was smaller than the critical value at 0.05 level of significance (2.3646). Therefore, the null hypothesis (H0): Mean X = Mean Y, was not rejected. The two sets of numbers were therefore not significantly different. This statistical analysis confirmed that the difference between individual samples was greater than the difference observed during the use of a fan. This procedure demonstrated that the electrical fan did not produce interfering PM_{10} nor have any impact on the smoke plume concentration.

Table 5.2. PM_{10} concentrations with and without influence of Fan

Background PM_{10} mass concentration ($\mu g\ m^{-3}$ of air)	Fan influenced PM_{10} mass concentration ($\mu g\ m^{-3}$ of air)
4.1	5.2
5.3	4.1
4.1	5.3
5.3	4.2
4.2	5.8
5.8	5.1

5.6 Agreement between Interspecific Smoke Signatures

Good agreement was noted between the mean quantitative smoke signatures of birch, poplar and pine; however, the mean quantitative spruce smoke signature was found to be twice as much as those of the other three wood types (Figure 5.11).

The difference between smoke signatures of spruce and other wood types

was initially thought to result from the difference in inherent characteristics amongst tree species; however, significant differences were not expected between spruce and pine because they are both coniferous and are closely related. After carefully considering all factors, the variation in the forms of firewood burned in the study was suspected to have caused the elevated quantities of guaiacol and derivatives: while the other 3 types of wood were cordwood, the spruce used in the study was dimensional lumber. Spruce is primarily used for construction purposes and is mostly processed into dimensional lumber for this purpose. Spruce cordwood is usually produced from "dead falls" and is often scarce. Subsequent literature review has supported the suspicion that the use of dimensional lumber had caused the increased guaiacol and derivatives quantities. Senf (1996) has reported that the use of dimensional lumber could reduce firewood combustion particulate matter by approximately 50% when compared with the results of cordwood. Unfortunately, no reason was provided; the phenomenon was possibly due to much lower moisture content and the relatively large surface area of dimensional lumber compared with cordwood. The influence of tree bark seems less likely because of its relatively small quantity. When this 50% factor is incorporated into the spruce smoke profile calculation, good inter-specific agreement was noted between spruce and other wood smoke signatures (Figure 5.12).

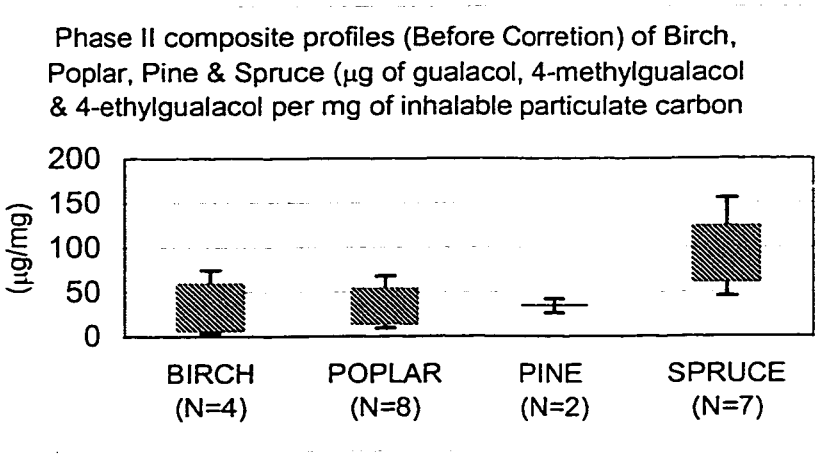


Figure 5.11 Comparison of smoke signatures of birch, poplar, pine and spruce (without correction)

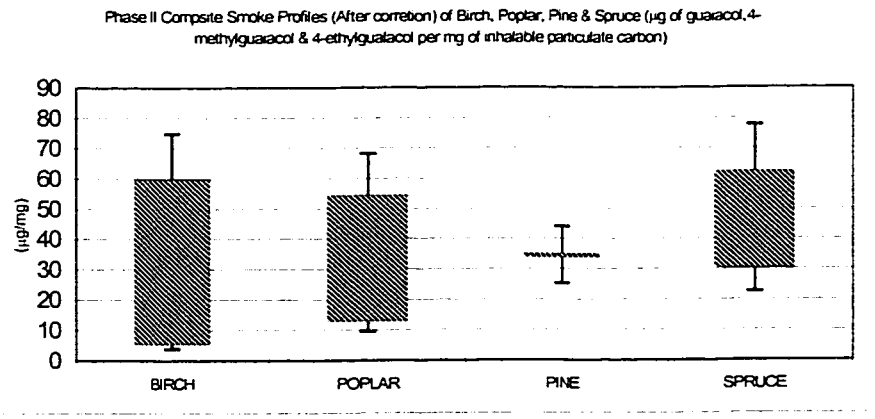


Figure 5.12 Comparison of smoke signatures (after corrections for using dimensional spruce lumber)

5.7 Positive Control – Fossil Fuel Exhaust

Some quantities of methoxylated phenols were noted in individual gasoline and diesel engine exhaust fume samples (Table A5 and Table A6). These concentrations were in the range of background levels (Table 5.3). For example, isoeugenol was approximately 2.4x and 4-methylguaiacol was 0.5x of the respective background concentrations as determined in control samples. Consequently, the detected methoxylated phenols were suspected to result from "carry-over" contamination on the sides of the PUF holders and were not combustion by-products of fossil fuels. In view of the low concentrations, the "carry-over" quantities, if any, did not significantly affect the rest of the experimental result.

Table 5.3 Comparison between fossil fuel fume sample contamination and background levels (Phase II)

Samples	Guaiacol (μg/mg)	4-methyl-guaiacol (μg/mg)	4-ethyl-guaiacol (μg/mg)	Isoeugenol (μg/mg)
Control (background)	0.22	0.11	0.15	0.22
Gasoline 1	<MDL	0.14	0.070	<MDL
Gasoline 2	<MDL	0.16	0.070	<MDL
Gasoline 3	<MDL	<MDL	<MDL	<MDL
Diesel 3	0.14	<MDL	<MDL	<MDL
Diesel 4	0.10	0.13	0.050	0.53

<MDL = below method detection limit

5.8 Comparison of Results with Literature Reports

A previous study has found that pine wood smoke, which is derived from coniferyl-type lignin and which is different from wood smoke derived from gymnosperm lignin, contains mainly vanillin and vanillic acid and lesser amounts of other pyrolysis products (Simonelt et al, 1993). While the limited number of pine smoke samples in Phase I reflected this pattern, this pattern was not repeated in the Phase II pine and spruce smoke samples.

Hawthorne and co-workers (1992) have suggested that the 3 major methoxylated phenols as a group, (guaiacol, 4-methylguaiacol and 4-ethylguaiacol) correlate well with the overall guaiacols content. They suggested

that these three major species alone could represent the overall guaiacols concentration in wood smoke. The findings in Phase I of this study are different from Phase II, in that while guaiacol always remains as the most abundant species, 4-methylguaiacol and 4-ethylguaiacol are sometimes missing from the smoke composition. On the other hand, vanillin can be abundant under certain conditions.

Pine wood smoke has been previously reported to contain mainly vanillin and vanillic acid and lesser amounts of other pyrolysis products because of its coniferyl-type lignin (Simonelt et al, 1993). The abundance of vanillin noted in Phase I spruce wood smoke samples, also a conifer species, suggests that vanillin can be a major species in soft wood smoke. Nevertheless, while pine and spruce are coniferyl, the production of vanillin was found to differ in this study. Reasons for the observed variation may be due to differences in moisture content, burn conditions and other unknown factors.

The quantitative smoke profiles (i.e. the total amount of the 3 major methoxylated pehnol species - guaiacol, 4-methylguaiacol, and 4-ethylguaiacol per mg of inhalable particulate carbon) of Phase II and the North Dakota study (Hawthorne et al. 1992) are tabulated in Table 5.4. As expected, variability exists.

Table 5.4 Chemical profiles determined in Phase II and N. Dakota Study

	Hawthorne et al. (1992)	This Study (Phase II)
Tracer species	μg/mg of carbon	μg/mg of carbon[a]
Guaiacol (G)	42	17
4-methylguaiacol	26	13
4-ethylguaiacol	12	5.0
G + methylG + ethylG	80	35

[a] values reported are average values of all samples; a 50% correction factor has been put in for spruce smoke signatures for using dimensional spruce lumber.

5.9 Summary of Results

5.9.1 Phase I

1. Variability was noted among smoke signatures, both between samples of the same wood, and between wood types. Poplar intra-specific samples were noted to have the most consistent patterns.
2. Vanillin was present in some samples of all wood species, but it was a major by-product only for some spruce smoke samples.
3. Quantitative interpretation was not possible due to the small sample number. An additional second phase was needed for proper data interpretation.

5.9.2 Phase II

1. Agreement was noted between composite smoke signatures of birch, poplar, and pine, both quantitatively and qualitatively.
2. Quantity of guaiacols in spruce wood smoke generally agreed with others after correcting for the use of dimensional spruce lumber.
3. Intra-specific variability exists between individual samples of same wood type but was generally much less than that which occurred in Phase I.
4. The three major species of methoxylated phenols, that is, guaiacol, 4-methylguaiacol and 4-ethylguaiacol comprised more than 90% of the overall methoxylated phenols analysed.
5. Generally, the 3 major species, in descending order, were guaiacol, 4-methylguaiacol and 4-ethylguaiacol.
6. Combustion of fossil fuels (gasoline and diesel) does not produce guaiacols in sufficient quantities to confound interpretation. The trace levels observed in a few samples was attributed to sampling contamination.

6. DISCUSSION

Wood combustion is a complex process because of the non-homogeneity of the fuel and the batch nature of the fuelling procedure. Findings in this study are consistent with the observation of McCrillis and Burnet (1990) that the quantity and diversity of the combustion by-products are influenced by combustion conditions, and by other known and unknown factors. Any attempt to characterize or to suggest a typical burn condition for any wood combustion process to be representative is unrealistic. Likewise, to predict results for typical burn conditions is not possible (Guenther, 1987). Consequently, it is not realistic to establish through a single bench top experiment a universal smoke signature which will be applicable to all apportionment processes, nor is it appropriate to rely on source composition libraries established in other studies (Mukeerjee and Biswas, 1992). To account for the variability resulting from inherent fuel characteristics and different combustion conditions, it will be necessary to establish a source profile each time at the actual smoke source for each individual apportionment study.

6.1 Variability

Differences were noted between the average wood smoke profiles obtained in the two phases of this study. While good agreement was noted among the composite smoke signatures of all of the studied wood types, variability among individual inter-specific smoke signature was noted. The variability of the smoke profile is expected. Rogge et al. (1998) have studied fine organic aerosols in wood smoke produced by combustion of pine and oak. They have reported that methoxylated phenols emission rates between pine and oak can vary as much as 100 fold. Although the North Dakota study (Hawthorne et al., 1992) successfully used a pre-determined composite smoke signature, findings of this study suggested that the application of a universal smoke profile is not always feasible due to the complexity of interacting conditions.

Potential sources of variability in the formation and diversity of combustion by-products are many. Most result from the inherent chemical characteristics of

the tree species, and just as significantly, the combustion conditions.

6.1.1 Chemistry of Wood

Difference in chemical compositions of tree species is a major source of variability. Wood is composed of approximately 30% lignin (Simonelt et al., 1993) which is derived primarily from *p*-coumaryl, coniferyl, and sinapyl alcohols (Grimshaw, 1976). The degradation products from oxidation or pyrolysis of these aromatic alcohols are classified as coumaryl, vanillyl, and syringyl moieties respectively (Hedges and Ertel, 1982). However, their proportions can vary considerably among the major plant classes. For instance, lignins of hardwoods (angiosperms) are rich in products from sinapyl alcohol. On the other hand, softwoods (sumnosperms) have a high proportion of products from coniferyl alcohol with only minor components from sinapyl alcohol.

6.1.2 Combustion Conditions

In addition to the inherent wood chemistry, combustion conditions also affect the formation of combustion by-products significantly. In general, two types of combustion conditions exist: hot burning and cool burning (Rau and Khalil, 1989). Hot burning is described as turbulent, brightly flaming combustion with an adequate, but not excessive, combustion air supply. On the other hand, cool burning is described as low turbulence, air starved, and smouldering combustion possibly with some smoky orange flames. Other than air supply, weather-related variables such as relative humidity and temperature also influence the combustion efficiency and the particle-vapour partitioning coefficient (K_p). According to Ward and Hardy (1989), the diversity of combustion products is largely influenced by the combustion conditions. McCrillis and Burnet (1990) have further suggested that wood smoke chemical profiles not only vary with wood species and burn-rate, but also depend on factors including the altitude where the combustion occurs. These factors not only affect the K_p of the semi-volatile organic compounds, they could in turn influence the formation and mass of suspended particles through the adsorption and volatilization of aerosol.

Moreover, the moisture content in biomass fuel can limit the rate of fuel consumption resulting in an increased formation of carbon monoxide and associated higher molecular weight hydrocarbon species (Ward and Hardy, 1989). In hot burning combustion, the organic carbon fraction of the particles is more completely consumed thereby creating a higher percentage of carbon dioxide. The high temperature generated during hot burning increases the degree of turbulence in the flame envelope. Turbulence in turn increases the entrainment of ash and contributes to the break-up of the ash material into more particulate matter (Ward and Hardy, 1989), while initially high intensity fires produce fewer fine particles in the emission (Ward et al., 1988). The production of particulate matter in fluctuating amounts can undoubtedly alter the smoke profile.

6.1.3 Particle-Vapour Partitioning

The particle-vapour partitioning (K_p) of the semi-volatile organic compounds contributes to variability. Some aerosol constituents exist in both gas and particle phases, and volatilization and sorption processes govern the partitioning process. The gas-solid distribution depends on atmospheric conditions such as temperature, content of water vapour and the vapour pressure of the particular constituent. Some inorganic compounds such as ammonium nitrate (Stelson and Seinfeld, 1982a; Bassett and Seinfeld, 1983, 1984) and some organic substances (Ligocki and Pankow, 1989; Pankow, 1994a and 1994b) are semi-volatile.

Temperature, by far, is the most influential factor on the partitioning coefficient (Lee and Tsay, 1994). Even diurnal temperature fluctuations can re-distribute these semi-volatile compounds between the gas and particle phases. Wood smoke contains a large number of these semi-volatile organic substances. The distribution of semi-volatile wood smoke tracer species, and hence the smoke signature, vary depending on the ambient temperature during the smoke sampling process.

Humidity is also known to have effects on the partition coefficient (K_p) of

semi-volatile organic substances such as PAHs (Lee and Tsay, 1994). Compared to temperature, the effect of humidity is relatively small when it is above 50%; however, Lee and Tsay (1994) have noted that the K_p of PAHs can triple when the relative humidity changes from 53% to 93%.

6.1.4 Formation Mechanisms of Particles

During the smoke sampling process, relationship between quantities of airborne particles and smoke tracers interacts and shifts continuously, compounding the variability further. Airborne particulate matter has many origins, and its formation is dynamic involving morphological, chemical, physical and thermodynamic processes. Wood combustion generates primary particles. However, secondary particulate matter can be formed from condensation of high temperature vapour or from vapours generated as a result of chemical reactions involving gas-phase precursors. The secondary formation processes can either cause the generation of new particles (Covert et al., 1992) or adding of material to the pre-existing particles (Wall et al., 1988; Wu and Okada, 1994). Both scenarios could drastically alter the mass concentration of the overall particles in the air and the relative concentrations of the smoke signature.

6.2 Uncertainty

It is a general assumption that the vapour-particle equilibrium is achieved in the atmosphere. Gerde and Scholander (1989) have predicted that the gas/particle equilibrium of semi-volatile substances takes minutes to hours to achieve. Nevertheless, the kinetics and dynamics of redistribution and transformation are not well understood.

Other sources of uncertainty also include the accuracy of equipment. It is assumed that the performance of equipment used in this study is consistent. However, this is not easily confirmed.

6.3 Cluster Analysis

Cluster Analysis was performed on the four smoke signatures to search

for relatively homogeneous groups. The characteristics of each smoke type is determined by seven variables, namely: guaiacol, 4-methylguaiacol, 4-ethylguaiacol, eugenol, vanillin, isoeugenol and acetovanillone. Each variable is defined as a separate cluster, or group. Smoke signatures with similar characteristics form clusters based on the distance between them. There are three basic types of distance measurements. This study uses the *Squared Euclidean Distance* equation to calculate the separation distance for each pair of objects and to form a distance matrix.

$$\text{Distance}(X,Y) = \sum_{I} (X_i - Y_i)^2$$

The *Squared Euclidean Dissimilarity Coefficient Matrix* provides a general picture of dissimilarity. The optimal value is 0 meaning that the two objects were identical. As the value of this distance increases to the right, the two objects being compared are becoming more different and are less likely to be grouped together.

The output of the cluster analysis is a dendrogram - a graphical depiction of the similarity and dissimilarity between the compared objects. A dendrogram (Figure 6.1) illustrates the clustering pattern of the smoke signatures. All distances have been scaled to range from 0 to 25. While the horizontal line represents the distance, the vertical line illustrates the linkage between two compared smoke profiles. The distance between Birch and Poplar is 0.0049, whereas the distance between Birch and Spruce is 0.2371. Therefore, Birch and Poplar are more similar and form a cluster. On the other hand, Pine is similar to Spruce and they form another cluster.

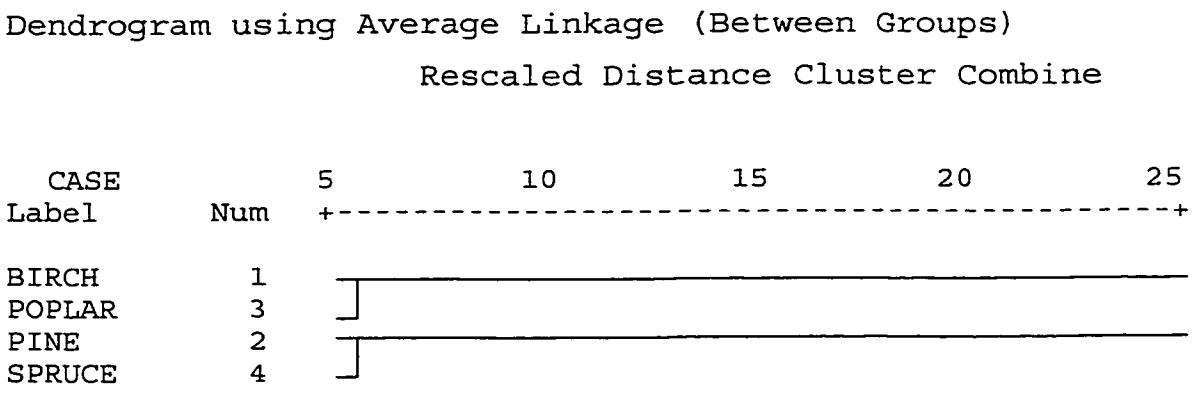


Figure 6.1 Cluster analysis Dendrogram of smoke signatures

This result confirms the previous discussion that lignins of hardwoods (angiosperms) and softwood (sumnosperms) are different. It further strengthens the hypothesis that chemistry of different tree species is a major source of variability, and that the establishment of a "universal" smoke signature for future use is not realistic where any mix of combustion wood types will arise.

6.4 Application

When used with region-specific source profiles, the receptor modelling may provide the best estimates of contributions from emissions sources that have distinctive source profiles (Lurmann 1989). This study has confirmed that guaiacol and derivatives are specific tracers for wood smoke. In spite of variability and uncertainty, the study results have demonstrated that smoke signatures based on guaiacols species can be used to apportion wood smoke employing receptor modelling. Data in this study have shown that vanillin could be a major guaiacol species in spruce wood smoke (Fig. 5.4), when wood is burned under certain combustion and ambient conditions. It is therefore recommended that in addition to guaiacol, 4-methylguaiacol and 4-ethylguaiacol, vanillin be included when establishing smoke signatures in future field apportionment processes, to account for variability. The inclusion of vanillin in smoke signatures, especially in Alberta regions where the wood waste is made up mainly of coniferous species, would enhance the accuracy of the same

contribution process.

6.4.1 Elimination of Nearby RWC Influence

Receptor models are unable to differentiate the impacts of various point sources from the same source groups due to the similarity of chemical compositions (Freeman et al., 1989). Other than wood residue burners, residential wood combustion (RWC), e.g. wood burning stoves and fireplaces, can be a major contributor of wood smoke. Obviously, it is essential to consider the impact of other smoke sources when apportioning the contribution of wood residue burners. During summertime, the impact of RWC is not a major concern because the level of RWC emissions is generally low; however, the impact of RWC generated in municipalities can be significant in wintertime.

The influence of RWC can be determined. The location of the smoke-monitoring device is an important determining factor. A previous study has found RWC smoke concentrations in various parts of town can vary up to fourfold. As expected, the highest readings are in the residential area (Heumann et al., 1991). Larson et al. (1990) also observed a similar spatial variability between RWC smoke concentrations. Summarizing various studies, Larson and Koenig (1994) have concluded that wood smoke concentrations are higher in residential areas than in downtown urban or industrial areas, and are generally higher at night than during the day. With this in mind, the influence of residential wood combustion, and the influence by a distant source, e.g. a wood residue burner, may be estimated by noting the difference between concentrations of chemical tracers in residential and downtown business areas.

This logic and strategy can be illustrated with a real example. A wood residue burner is located south of the Town of High Level, Alberta, as shown in Figure 6.1. The business area is located in the south-eastern section of the town, while service facilities such as a school, hospital and recreational facilities are located in the western section of the town. Monitors can be set up in the residential, business and service areas. It is assumed that wood smoke from the residue burner equally impacts these areas. The residential area, in addition, is

further impacted by RWC. By noting the difference between the tracer concentrations in the residential area and areas not substantially impacted by RWC, influence from the wood burner can be estimated.

One might be tempted to apportion wood smoke during the warmer day time hours while the RWC impact is insignificant. However, we should keep in mind that we are most concerned with human exposure to wood smoke when its vertical dispersal is limited by inversion during cold, calm nights. Exposure assessment performed during in the daytime may not serve the purpose of health risk assessment.

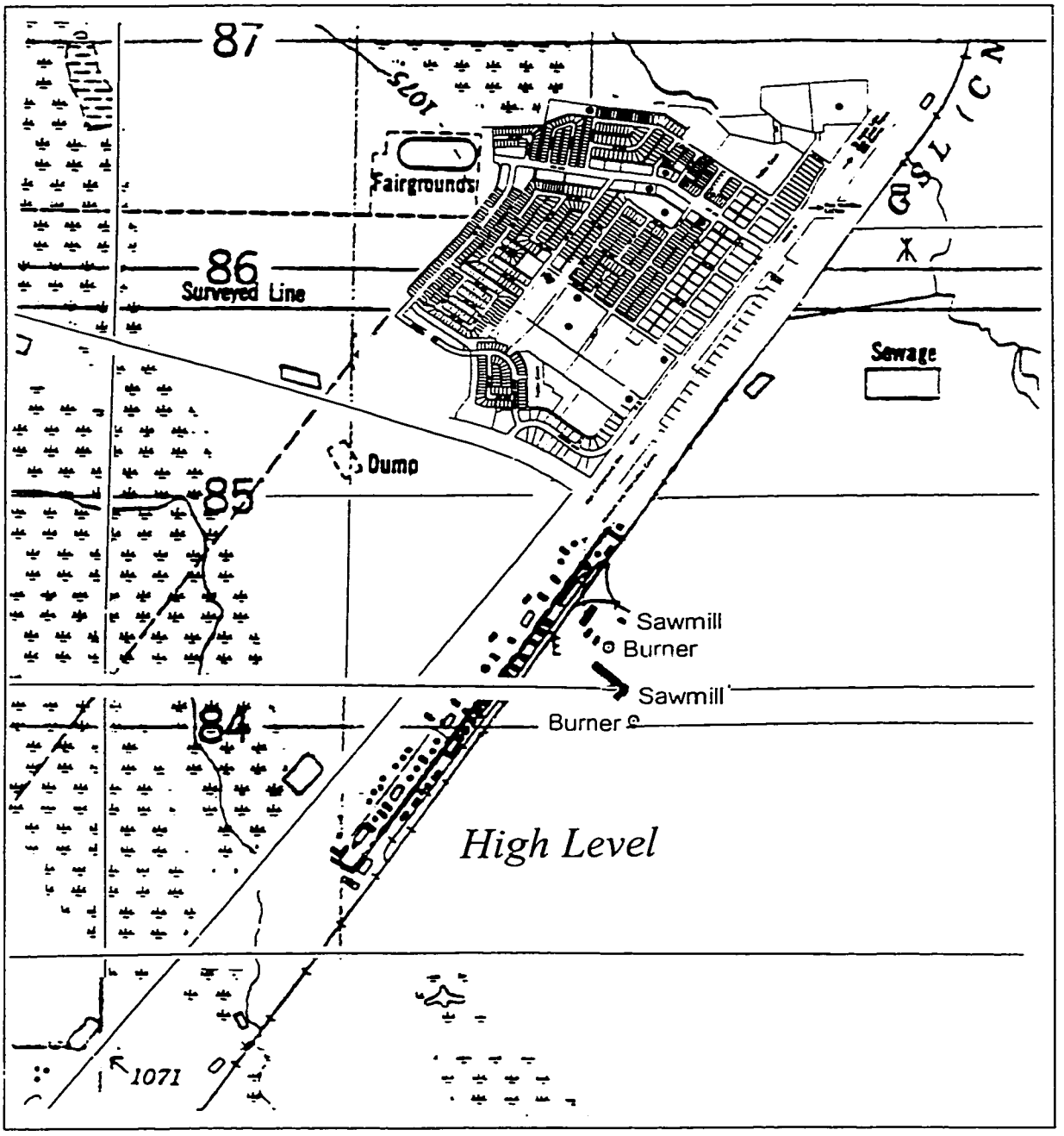


Figure 6.2 Locations of Town of High Level and Wood Waste Burners

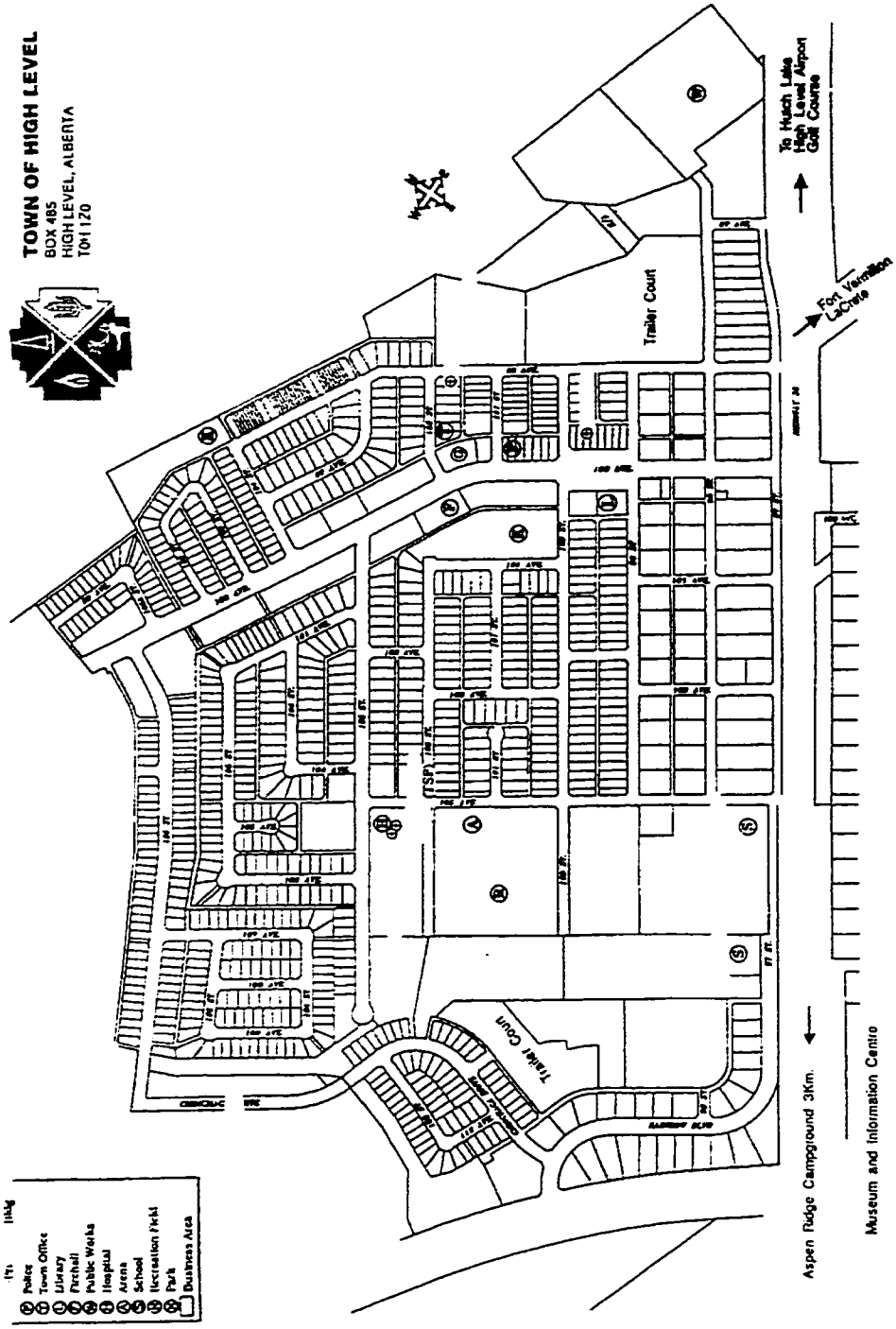


Figure 6.3 Map of the Town of High Level

6.4.2 Cautions about Using Quartz Filters

Quartz filters are the only known filters suitable for the determination of the carbon content of particulate matter. Unfortunately their moisture-absorbent nature makes them difficult to handle. The significant loss of filter material during the loading and unloading procedures in this study has rendered the PM_{10} mass concentration not usable. To minimize filter material loss, immediate unloading of filters is not recommended. Loaded impactors after one sampling should be left undisturbed, allowed to dry, then unloaded the following day. Nevertheless, in an actual smoke signature determination process, it is expected that the moisture content from the smoke would have a lesser impact on the filters due to greater distance between source and monitoring equipment resulting in lower humidity of sampled air. This distance facilitates a further decrease in smoke humidity compared with the source sampling technique that was employed in this case.

6.4.3 Cautions about Selecting Airflow Calibrators

A bubble flow meter was used to verify the air pump flow-rate. The use of a "wet" flow meter proved to be problematic, and it was a major potential source of experimental errors and filter contamination. To confirm the flow-rate, it was often necessary to obtain up to 10 or more consecutive readings from the bubble flow meter. Consequently, bubbles and detergent were noted migrating to the distal tip of the hose connecting the meter and the calibration cap, causing contamination of the impactor. A "dry" calibrator is highly recommended to prevent filter contamination. Additionally, the sub-zero ambient temperature likely has less impact on "dry" calibrators.

7. CONCLUSIONS

7.1 Validation of Methylated Phenols as Tracers

The validity of air contaminant emissions tracers rests upon a number of important assumptions (Currie et al. 1994): conservation of the tracer, knowledge of source identity, closure of system under study, and specificity of the tracer to the source in question. Findings in this study have provided information/evidence to support the proposed use of methoxylated phenols as tracers of source apportionment tracers.

7.1.1 Conservation

Based on PAHs studies by Kamens and co-workers (1986; 1987), and Nielsen et al. (1983), reaction rates of organic combustion by-products, likely including methoxylated phenols, are probably negligible at low ambient temperature.

Circumstantial evidence provided by Steiber and Dorsey (1990) and more recently by Hawthorne et al. (1992) suggests that this methoxylated phenol tracer group is relatively stable, at least in winter.

7.1.2 Known source

Positive control samples from fossil fuel combustion (gasoline and diesel) have confirmed that the methoxylated phenol tracer group is specific to wood or other biomass burning among major fuel emission sources. Other major sources of ambient methoxylated phenols are not known.

7.1.3 Closed system

Influence of biomass smoke, such as from forest fires, resulting from long range transport can be recognized by simply noting the background tracer concentrations upwind from the source under study.

Receptor modelling cannot differentiate sources of similar origin, e.g. wood smoke from wood residue burner and wood smoke from RWC; however, the influence from RWC may be determined by carefully selecting discriminating

monitoring locations, e.g. downtown or industrial area that has less influence from RWC.

7.1.4 Uniqueness

Methoxylated phenols are unique to wood combustion because they are a direct consequence of the destruction of the lignin structure (Steiber et al., 1992).

Methoxylated phenols are not by-products of fossil fuel combustion.

7.2 Application to RWC Apportionment

The apportionment of smoke emitted from industrial wood residue burner is feasible using methoxylated phenols because of their stability, and their uniqueness; however, methoxylated phenols are not useful for apportioning community RWC sources. As discussed above, wood combustion by-products may be influenced greatly by the wood type, as well as by the combustion conditions. In homes, individuals prefer different types of firewood, and the burn conditions differ according to individual needs and preference. In reality, a composite profile representative of average RWC emissions of numerous residences in an area is difficult to develop (Kowalczyk and Green, 1982; Watson, 1979).

7.3 Future Research

Variability of source profiles and degradation of organic compounds after release continue to plague the field (Gordon, 1988). Conservation (i.e. linearity), stability and decomposition of organic tracers should be investigated. This concern has led to the discontinued use of levoglucosan as a wood tracer. Further research to verify transformation of its conversion is needed.

Similarly, the ability to distinguish softwood from hardwood emissions using retene or other tracers may be valuable in certain cases. it is necessary to investigate the suggestion (Steiber and Dorsey, 1990) that any fuel rich in aromatics may produce retene rendering it not suitable to apportion softwood smoke .

Combustion conditions employed in this study were relatively controlled. The question as to whether the production of methoxylated phenols is independent of burn conditions remains unanswered. Hawthorne et al. (1989) have suggested that conversions among guaiacol species may explain the relatively consistent total methoxylated phenols quantities, in spite of the use of various wood types and burn conditions. The answer to this question may prove to be the key to developing a reliable methodology to apportion RWC where "average burn conditions" do not exist. Further research in this aspect is needed.

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Appendix

Table A1 Data Summary for Phase I (after blank subtraction)

	Carbon on filter (mg)	Guaiacol (μg)	4-methylG (μg)	4-ethylG (μg)	Eugenol (μg)	Vanillin (μg)	Iso-eugenol (μg)	Aceto-vanillone (μg)
Birch 1*	1.4	—	—	—	—	—	—	—
Birch 2*	7.6	—	—	—	—	—	—	—
Birch 3	0.13	0.77	0.12	0.12	NQ	0.46	NQ	NQ
Birch 4	0.37	5.1	0.74	0.36	NQ	0.39	NQ	NQ
Birch 5	0.14	1.7	0.23	0.27	NQ	0.27	0.41	NQ
Poplar 1	0.18	9.6	2.7	1.4	NQ	0.48	NQ	NQ
Poplar 2	0.14	6.8	1.9	2.0	NQ	0.23	NQ	0.050
Poplar 3	0.49	18	3.6	3.4	9.0	0.49	0.20	0.13
Poplar 4	0.14	8.2	1.6	1.6	0.65	0.30	NQ	0.050
Poplar 5*	0.36	—	—	—	—	—	—	—
Pine 1	0.21	0.46	0.080	0.030	NQ	NQ	NQ	NQ
Pine 2	0.14	0.36	0.040	NQ	NQ	0.15	NQ	0.030
Pine 3	0.90	3.5	2.2	0.47	NQ	0.070	NQ	NQ
Pine 4	0.97	1.4	0.89	0.40	0.18	NQ	NQ	0.14
Pine 5	0.91	0.43	NQ	0.070	NQ	NQ	NQ	NQ
Spruce 1	0.15	0.29	0.050	NQ	NQ	0.23	NQ	0.050
Spruce 2	0.53	0.44	NQ	NQ	0.090	0.29	NQ	NQ
Spruce 3	0.38	0.76	0.27	0.070	0.11	NQ	NQ	NQ
Spruc4*	0.59	—	—	—	—	—	—	—
Spruc5[b]	—	—	—	—	—	—	—	—

NQ = not quantified, after blank subtraction, value was 0 or <0
[b] = uneven particulate collection, data not used
* = GC/MS data lost

Table A2a Data summary for Phase II (before blank subtraction)

	Carbon on filter (mg)	Guaiacol (μg)	4-methylG (μg)	4-ethylG (μg)	Eugenol (μg)	Vanillin (μg)	Iso-eugenol (μg)	Aceto-vanillone (μg)
Birch 1*[u]	0.090	—	—	—	—	—	—	—
Birch 2*[u]	0.26	—	—	—	—	—	—	—
Birch 3[u]	0.13	1.1	0.78	0.37	<MDL	1.6	<MDL	0.064
Birch 4	0.47	1.6	0.98	0.36	<MDL	1.7	0.027	<MDL
Birch 5	0.30	3.2	1.3	0.41	<MDL	1.6	0.63	<MDL
Birch 6[u]	0.17	7.5	6.1	2.6	<MDL	3.6	<MDL	<MDL
Birch 7*	1.1	—	—	—	—	—	—	—
Birch 8	0.84	27	17	4.9	<MDL	3.3	0.43	0.41
Birch 9[u]	0.26	4.2	2.7	1.7	<MDL	2.4	0.12	0.24
Birch 10	0.30	2.7	1.3	0.95	<MDL	4.0	0.043	0.30
Poplar 1*	0.45	—	—	—	—	—	—	—
Poplar 2	0.41	5.0	2.0	0.99	<MDL	1.3	<MDL	0.10
Poplar 3	0.18	3.7	1.6	0.60	<MDL	2.3	0.019	0.14
Poplar 4	0.13	2.5	1.4	0.47	<MDL	0.44	0.041	<MDL
Poplar 5	0.23	3.4	0.96	0.26	<MDL	0.98	0.034	0.087
Poplar 6*	0.14	—	—	—	—	—	—	—
Poplar 7	0.23	4.8	4.3	2.2	0.15	0.82	<MDL	<MDL
Poplar 8	1.6	8.8	8.0	3.3	<MDL	<MDL	<MDL	<MDL
Poplar 9	1.0	34	11	8.4	<MDL	<MDL	<MDL	<MDL
Poplar10	1.4	31	18	10	0.65	2.0	0.19	0.34
Pine 1*	2.9	—	—	—	—	—	—	—
Pine 2*	2.1	—	—	—	—	—	—	—
Pine 3*[u]	0.29	—	—	—	—	—	—	—
Pine 4[u]	0.44	5.0	6.1	1.9	<MDL	0.66	<MDL	0.14
Pine 5[u]	0.53	16	13	4.5	<MDL	0.68	<MDL	0.072
Pine 6	0.56	8.2	7.8	3.3	<MDL	1.5	<MDL	0.11
Pine 7	0.39	5.7	5.2	1.9	<MDL	0.47	<MDL	0.036
Pine 8*	0.39	—	—	—	—	—	—	—
Pine 9*	0.92	—	—	—	—	—	—	—
Pine 10*	1.3	—	—	—	—	—	—	—
Spruce1*	2.3	—	—	—	—	—	—	—
Spruce 2	1.3	62	68	31	5.6	0.97	0.78	<MDL
Spruce 3	0.90	39	46	17	2.0	1.9	0.25	0.39
Spruce4[u]	0.63	120	200	23	1.6	2.6	2.2	0.33
Spruce 5	1.1	33	33	9.6	0.35	4.1	1.6	0.60
Spruce 6	2.2	56	57	21	6.6	9.0	0.92	1.8
Spruce 7	3.7	100	92	36	22	4.5	0.44	0.64
Spruce8*	0.56	—	—	—	—	—	—	—
Spruce 9	0.52	18	17	4.6	<MDL	3.0	0.21	0.28
Spruc10	0.40	13	14	4.1	<MDL	2.4	<MDL	0.19
PUF Field Control 2		0.067	0.029	0.035	<MDL	0.40	0.027	0.052
PUF Field Control 3		0.068	0.030	0.027	<MDL	1.6	0.55	0.18
PUF Field Control 4		<MDL	0.040	0.042	0.012	<MDL	<MDL	0.078
Field Cont. average		0.045	0.033	0.035	0.0040	0.66	0.19	0.10
PUF Lab Blank 1		0.29	0.11	0.20	<MDL	5.2	<MDL	3.5
PUF Lab Blank 2		0.057	0.036	0.021	<MDL	0.74	0.050	<MDL
Lab Blank average		0.17	0.075	0.11	<MDL	3.0	0.025	1.7
PM filter blank 1	0.027							
PM filter blank 2	0.055							
PM filter blank 3	0.019							
PM filter blank 4	0.029							
PM filter blank 5	0.023							
Blank Subtraction[b]	**0.031**	**0.22**	**0.11**	**0.14**	**0.0040**	**3.6**	**0.22**	**1.8**

<MDL = below method detection limit (see Table 4.1)
[u] = uneven particulate collection, data not used
* = GC/MS data lost
[b] carbon blank subtraction = mean value of PM filter blanks
methoxylated phenol blank subtraction = sum of averages of field and lab controls

Table A2b Data summary for Phase II (after blank subtraction)

	Carbon on filter (mg)	Guaiacol (μg)	4-methylG (μg)	4-ethylG (μg)	Eugenol (μg)	Vanillin (μg)	Iso-eugenol (μg)	Aceto-vanillone (μg)	G + methylG + ethylG per mg carbon
BLANK	**0.031**	**0.22**	**0.11**	**0.14**	**0.0040**	**3.6**	**0.22**	**1.8**	
Birch 1*[u]	0.059	—	—	—	—	—	—	—	—
Birch 2*[u]	0.23	—	—	—	—	—	—	—	—
Birch 3[u]	0.094	0.88	0.67	0.23	<MDL	NQ	<MDL	NQ	—
Birch 4	0.44	1.4	0.88	0.22	<MDL	NQ	NQ	<MDL	5.2
Birch 5	0.27	3.0	1.2	0.27	<MDL	NQ	0.41	<MDL	16
Birch 6[u]	0.14	7.3	6.0	2.4	<MDL	NQ	<MDL	<MDL	—
Birch 7*	1.1	—	—	—	—	—	—	—	—
Birch 8	0.81	27	17	4.7	<MDL	NQ	0.21	NQ	59
Birch 9[u]	0.23	4.0	2.6	1.6	<MDL	NQ	NQ	NQ	—
Birch 10	0.27	2.5	1.2	0.80	<MDL	0.35	NQ	NQ	16
									Mean = 24
									SD = 24
Poplar 1*	0.42	—	—	—	—	—	—	—	—
Poplar 2	0.38	4.8	1.9	0.84	<MDL	NQ	<MDL	NQ	20
Poplar 3	0.15	3.5	1.5	0.45	<MDL	NQ	NQ	NQ	36
Poplar 4	0.098	2.3	1.2	0.32	<MDL	NQ	NQ	<MDL	37
Poplar 5	0.20	3.2	0.85	0.11	<MDL	NQ	NQ	NQ	—
Poplar 6*	0.11	—	—	—	—	—	—	—	—
Poplar 7	0.20	4.6	4.2	2.1	0.15	NQ	<MDL	<MDL	54
Poplar 8	1.5	8.6	7.9	3.2	<MDL	<MDL	<MDL	<MDL	13
Poplar 9	0.98	34	11	8.3	<MDL	<MDL	<MDL	<MDL	54
Poplar10	1.3	31	18	10	0.64	NQ	NQ	NQ	—
									MEAN = 36
									SD = 17
Pine 1*	2.9	—	—	—	—	—	—	—	—
Pine 2*	2.0	—	—	—	—	—	—	—	—
Pine 3*[u]	0.26	—	—	—	—	—	—	—	—
Pine 4[u]	0.41	5.0	6.0	1.7	<MDL	NQ	<MDL	NQ	—
Pine 5[u]	0.50	16	13	4.3	<MDL	NQ	<MDL	NQ	—
Pine 6	0.53	8.0	7.7	3.2	<MDL	NQ	<MDL	NQ	36
Pine 7	0.36	5.5	5.1	1.8	<MDL	NQ	<MDL	NQ	34
Pine 8*	0.36	—	—	—	—	—	—	—	—
Pine 9*	0.89	—	—	—	—	—	—	—	—
Pine 10*	1.3	—	—	—	—	—	—	—	—
									MEAN = 35
									SD = 0.99
Spruce1*	2.3	—	—	—	—	—	—	—	122
Spruce 2	1.3	62	67	31	5.6	NQ	0.56	<MDL	119
Spruce 3	0.86	39	46	17	2.0	NQ	0.033	NQ	—
Spruce4[u]	0.60	120	200	22	1.6	NQ	2.0	NQ	—
Spruce 5	1.1	33	33	9.5	0.35	NQ	1.3	NQ	68
Spruce 6	2.2	56	57	21	6.6	5.4	0.70	NQ	60
Spruce 7	3.6	100	91	36	21	0.82	0.22	NQ	63
Spruce8*	0.53	—	—	—	—	—	—	—	—
Spruce 9	0.49	18	17	4.4	<MDL	NQ	NQ	NQ	79
Spruc10	0.36	13	13	4.0	<MDL	NQ	<MDL	NQ	83
									MEAN = 85
									SD = 26

<MDL = below method detection limit (see Table 4.1)
NQ = not quantitified, after blank subtraction, value was 0 or <0
[u] = uneven particulate collection, data not used
* = GC/MS data lost

Table A3a Data summary for fossil fuels Exhaust in Phase II (before blank subtraction)

	Guaiacol (μg)	4-methylG (μg)	4-ethylG (μg)	Eugenol (μg)	Vanillin (μg)	Iso-eugenol (μg)	Aceto-vanillone (μg)
Gas 1	0.19	0.25	0.21	<MDL	0.20	0.038	0.10
Gas 2	0.18	0.26	0.16	<MDL	0.41	<MDL	<MDL
Gas 3	0.14	<MDL	0.10	<MDL	0.51	0.88	0.083
Gas 4	0.17	<MDL	0.033	<MDL	0.43	<MDL	<MDL
Diesel 1*	—	—	—	—	—	—	—
Diesel 2	0.15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Diesel 3	0.36	<MDL	0.048	<MDL	0.62	<MDL	<MDL
Diesel 4	0.32	0.23	0.19	<MDL	0.44	0.75	<MDL

<MDL = below method detection limit (see Table 4.1)
U = uneven particulate collection, data not used
* = GC/MS data lost

Table A3b Data summary for fossil fuels exhaust in Phase II (after blank subtraction)

	Guaiacol (μg)	4-methylG (μg)	4-ethylG (μg)	Eugenol (μg)	Vanillin (μg)	Iso-eugenol (μg)	Aceto-vanillone (μg)
BLANK	**0.22**	**0.11**	**0.14**	**0.0040**	**3.6**	**0.22**	**1.8**
Gas 1	NQ	0.14	0.067	<MDL	<MDL	NQ	NQ
Gas 2	NQ	0.16	0.010	<MDL	<MDL	<MDL	<MDL
Gas 3	NQ	<MDL	<MDL	<MDL	<MDL	NQ	NQ
Gas 4	NQ	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Diesel 1*	—	—	—	—		—	—
Diesel 2	NQ	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Diesel 3	0.14	<MDL	NQ	<MDL	NQ	<MDL	<MDL
Diesel 4	0.10	0.13	0.049	<MDL	NQ	0.53	<MDL

<MDL = below method detection limit (see Table 4.1)
NQ = not quantitified, after blank subtraction, value was 0 or <0
U = uneven particulate collection, data not used
* = GC/MS data lost