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**Fundamental Mass Transfer Modeling of
Emission of Volatile
Organic Compounds from Building Materials**

By

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A thesis submitted to

The Faculty of Graduate Study and Research

In partial fulfillment of the requirements for the

Degree of Doctor of Philosophy (Ph. D.) of Engineering

Department of Mechanical and Aerospace Engineering

Ottawa-Carleton Institute for Mechanical and Aerospace Engineering

Carleton University

Ottawa, Canada

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**Fundamental Mass Transfer Modeling of
Emission of Volatile
Organic Compounds from Building Materials**

Submitted by

Awad Bodalal

In partial fulfillment of the requirements for
the degree of Doctor of Philosophy of Engineering

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Abstract

In this study, a mass transfer theory based model is presented for characterizing the VOC emissions from building materials. A 3-D diffusion model is developed to describe the emissions of volatile organic compounds (VOCs) from individual sources. Then the formulation is extended to include the emissions from composite sources (*system comprising an assemblage of individual sources*). The key parameters for the model (*The diffusion coefficient of the VOC in the source material D , and the equilibrium partition coefficient k_e*) were determined independently (*model parameters are determined without the use of chamber emission data*). This procedure eliminated to a large extent the need for emission testing using environmental chambers, which is costly, time consuming, and may be subject to confounding sink effects.

An experimental method is developed and implemented to measure directly the internal diffusion (D) and partition coefficients (k_e). The use of the method is illustrated for three types of VOC's: (i) *Aliphatic Hydrocarbons*, (ii) *Aromatic Hydrocarbons* and (iii) *Aldehydes*, through typical dry building materials (*carpet, plywood, particleboard, vinyl floor tile, gypsum board, sub-floor tile and OSB*). Then correlations for predicting D and k_e based solely on commonly available properties such as molecular weight and vapour pressure were proposed for each product and type of VOC. These correlations can be used to estimate the D and k_e when direct measurement data are not available, and thus facilitate the prediction of VOC emissions from the building materials using mass

transfer theory. The VOC emissions from a sub-floor material (*made of the recycled automobile tires*), and a particleboard are measured and predicted.

Finally, a mathematical model to predict the diffusion coefficient through complex sources (*floor adhesive*) as a function of time was developed. Then this model (*for diffusion coefficient in complex sources*) was used to predict the emission rate from material system (*namely, substrate // glue // vinyl tile*).

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NOMENCLATURE

<i>A</i>	Area of the specimen (m^2)
<i>ACH</i>	Air change per hour (hr^{-1})
<i>B_{pt}</i>	Boiling Point of the compound ($^{\circ}C$)
<i>C</i>	Concentration of the compound within the solid specimen (mg/m^3)
<i>C₀</i>	Initial Concentration of the compound in the specimen (mg/m^3)
<i>C_e</i>	The equilibrium concentration (mg/m^3)
<i>c</i>	Concentration of the compound in the chamber air (mg/m^3)
<i>c₀</i>	Initial Concentration of the compound in the chamber air (mg/m^3)
<i>D</i>	Diffusion coefficient of the compound within the specimen (m^2/s)
<i>D_{eq}</i>	The equivalent diffusivity (m^2/s)
<i>D_p</i>	Diffusion Coefficient through the plywood (m^2/s)
<i>D_r</i>	Diffusion Coefficient through the Recycled Tires Tile (m^2/s)
<i>E_x</i>	Mass emitted from x-y plane
<i>E_y</i>	Mass emitted from y-z plane
<i>E_z</i>	Mass emitted from z-x plane
<i>FID</i>	Flame ionization detector
<i>FLEC</i>	Field and Laboratory Emission Cell
<i>GC</i>	Gas chromatograph

<i>GC/MS</i>	Gas chromatograph with a mass spectrometer analyzer
<i>h</i>	Convective mass transfer coefficient, (<i>m/hr</i>)
<i>HCA</i>	Hydrocarbon analyzer
<i>IRC</i>	Institute for Research in Construction
<i>IAQ</i>	Indoor Air Quality
<i>k_e</i>	Equilibrium Partition coefficient between the specimen and the air
<i>k_{r/p}</i>	The partition coefficient between the Recycled tires tile and the Plywood
<i>k_{r/air}</i>	The partition coefficient between the Recycled tires tile and the air
<i>k_{p/air}</i>	The partition coefficient between the Plywood and the air
<i>k_a</i>	The adsorption rate constant (<i>m/hr</i>)
<i>k_d</i>	The desorption rate constant (<i>l/hr</i>)
<i>K_e</i>	An equilibrium constant $K_e = k_a/k_d$ (<i>m</i>)
<i>L</i>	Chamber Loading Factor (<i>m⁻¹</i>)
<i>l</i>	Thickness of the specimen under investigation (<i>m</i>).
<i>LPM</i>	Liters per minute
<i>Mw</i>	Molecular Weight of the compound.
<i>M_e</i>	The equilibrium mass <u>on</u> the sink (<i>mg/m²</i>)
<i>m_{in}</i>	Mass entering to the chamber (<i>assume perfectly clean air supply, m_{in} = 0</i>)
<i>m_{sink}</i>	Mass rate adsorbed by the sink (<i>mg/hr</i>)
<i>m_{accum}</i>	Mass rate accumulated in the chamber air (<i>mg/hr</i>)
<i>m_{out}</i>	Mass rate leaving the chamber through the air exchange flow (<i>mg/hr</i>)
<i>m_{emitted}</i>	The rate of mass emitted by the source (<i>mg/hr</i>)
<i>m_{accumsink}</i>	The rate of mass accumulated at the sink surface

<i>N</i>	Air Change per hour (hr^{-1})
<i>NRC</i>	National Research Council of Canada
<i>ODE</i>	Ordinary Differential Equation
<i>OSB</i>	Oriented Strand Board
<i>P</i>	Laplace-Carson Transformation operator.
<i>Q</i>	Air flow rate into and out of test chamber, (m^3/hr)
q_1	First positive root of the characteristic equation
<i>r</i>	Slope of the straight line ($r = -q_1 D/L^2$).
<i>R</i>	Emission rate per unit area, ($mg/m^2 hr$)
<i>Re</i>	Reynolds number, ($Re = v \cdot x / \nu$)
<i>RH</i>	Relative Humidity
<i>RT</i>	Retention time (<i>min.</i>)
<i>S,s</i>	Transformation of <i>C</i> and <i>c</i> respectively.
<i>Sc</i>	Schmidt number ($Sc = \nu / D$)
<i>Sh</i>	Sherwood number ($Sh = h_D \cdot x / D$)
<i>SBR</i>	Styrene butadiene rubber
<i>T</i>	Temperature
<i>THC</i>	Total hydrocarbons
<i>TVOC</i>	Total volatile organic compounds
<i>t</i>	Time (s).
<i>u</i>	Intercept of the straight line ($u = \ln(c_2 - c_1)/c_0$).
<i>V</i>	Volume of the chamber air (m^3).
<i>VOC</i>	Volatile Organic Compound.

x	Linear distance (m)
Y	The concentration of VOC's in the test chamber
y	Linear distance (m)
z	Linear distance (m)

Greek Symbols

Δx	Distance step size in x-direction (m)
Δy	Distance step size in y-direction (m)
Δz	Distance step size in z-direction (m)
α	Variable ($\alpha = k_c A / V$)
β	Variable ($\beta = I h C_{sat}$)
δ	Boundary Layer Thickness (m)
π	Constant (22/7)
ρ	Density (mg/m^3)
ν	Kinematic viscosity of the air (m^2/sec)

Subscripts

i	Nodal point value
j	Nodal point value
k	Nodal point value

Chapter I

OVERVIEW

1.1 BACKGROUND

The "sick building syndrome" is an effect of many synergistic conditions of the indoor environment. One of these conditions is the presence of irritants in indoor air. These may have a number of origins, for example fumes from photocopiers, tobacco smoke, or various volatile organic compounds (VOC's) emitted from construction and furnishing materials.

In recent years, gradual and sometimes abrupt changes have taken place in people's life styles and in their homes and workplaces. The demand for improved housing for an increasing population with increased living standards soon outstripped the ability to meet it with traditional building materials such as natural woods. Increasing labor costs led builders to seek alternative materials that were cheaper and could be mass-produced and processed. For example, pressed-wood products and fiberboard were

routinely incorporated into new home construction. Household furnishing also changed in composition as plastics and artificial fibers gained acceptance. Household products such as cleaners, insecticides, and personal health care and grooming aid products introduced a host of new synthetic chemicals into the home environment with unknown effects on IAQ and the health of the occupants. Unlike the people in the workplace, a typical family of house occupants can be assumed to display a wide range of ages, body weights, states of health and toxicological susceptibilities: the list ranging from relative insensitivity to hypersensitivity. Furthermore, the levels of activity will vary considerably: from highly active to sleeping over the period of exposure. In 1984, it was hypothesized that the introduction of chlorinated organic compounds and other chemicals such as phthalate ester plasticizers into our homes, workplaces, and transport vehicles may be associated with an observed decline in mean sperm density (Murature et. al. 1984). And recently (1998) the data gathered from eight industrial countries including Canada showed an alarming decline in the number of male babies versus female, the researchers believe the main cause of this imbalance trend is the environment pollution including the indoor air.

A worldwide energy crisis occurred in 1973-1974. Suddenly, the cost per barrel of crude oil jumped from \$3 to \$30, and overnight people began to worry about the cost of heating their homes and offices. To save energy, building owners and operators began to tighten structures to reduce the infiltration of outside air to reduce the energy expenditure needed to heat or cool it to the desired temperature. Utilities began promoting

their own residential energy conservation programs, with subsidies given to participating homeowners. The more energy efficient and airtight house was perceived as a more desirable and saleable commodity. Buildings became better insulated, and these barriers to the exchange of heat and air between the building and the outside environment led to what we now call the tight building syndrome (TBS). This decrease in the number of air changes per hour (ACH) led to an increase in concentration of the building contaminants that had been emitted indoors.

The concentrations of VOCs due to emission are usually quite low. However, a number of factors suggest that this would not necessarily mean that the risk to human health is low. It is believed that the sensory reaction of the human body to odorous substances in our surroundings in many cases is proportional to the logarithm of the exposure to the specific irritant (Berglund 1985). Another factor stressing the risk of VOCs is long exposure even at low concentrations. With regard to exposure to Carcinogens, multiple exposure to lower concentrations may be even more harmful than exposure to isolated peak concentrations (Holmberg, 1977).

The construction and furnishing materials that do not contain any VOCs will also play a role in the "sick building" although they are not the primary emission sources of VOCs. A material in contact with indoor air will act as an adsorbing material as long as the concentration of the specific compound in the air is higher than the corresponding gas phase equilibrium concentration within the material. When the concentration in the air

later decreases due to ventilation, the material will become an emitting source of the compound as the concentration in balance has reversed. In this way the material behaves as a capacitor temporarily storing the compound and then re-emitting it, thereby delaying the expulsion of the volatiles from the building. Slow emission (*if the volatile has been absorbed deeply into the material*) can result in undesirable concentrations of VOCs in indoor air for a long period of time.

The recognition that the quality of indoor air can be worse than that of outdoor air due to a number of pollutants, especially volatile organic compounds (VOCs) (De Bortoli et al. 1986 and Wallace et al. 1987), has motivated the research on the sources of such compounds. After a considerable number of complaints regarding the quality of indoor air in new and freshly renovated buildings, vapours emitted from two types of sources, namely building and furnishing materials on the one hand and household products on the other, have been the subject of investigation at various laboratories in recent years (Molhave 1982, Knoppel et al 1991 and Baldwin et al. 1990). Some engineers and building owners who design and operate the buildings argue that these complaints are psychosomatic, since they have complied with the “*standards*” and they have provided the required ventilation rate. However, according to the existing standards, the human is considered to be the primary source of the pollution (*human activity*). In other words the recommended required ventilation rate is based on the assumption that the mechanical ventilation system, building materials, and furniture are considered to be clean (*the meaning of this assumption is that if*

the people were taken away from the building then the indoor air quality should be the same as the outdoor air).

The contribution made by building and furnishing materials to indoor air pollution has been demonstrated by a study of VOC emission in four newly built, unoccupied test houses (Yu et al. 1997) (See Table 1-1). A maximum TVOC concentration of $9700 \mu\text{g}/\text{m}^3$ was measured during the first month of monitoring of the test houses; after 6 months these concentrations declined to about $800 \mu\text{g}/\text{m}^3$ and after about 1 year to about $600 \mu\text{g}/\text{m}^3$. After 18 months a more or less steady concentration of $200 \mu\text{g}/\text{m}^3$ was attained. This shows the negative impact that the renovations and construction activities have on the indoor air quality. The emission rate data obtained in this type of research are of considerable interest, both for estimating the population exposure to such vapours and for the selection by architects and engineers of the safest building and furnishing materials.

Table 1.1 The Effects of Renovations on the TVOC Concentration

<i>Number of Months from Renovation</i>	<i>TVOC Concentration ($\mu\text{g}/\text{m}^3$)</i>	<i>Number of Compounds Detected</i>
1	9700	254
6	800	200
12	600	71
18	200	71

Increasing ventilation rate (*Solving the Indoor Pollution by Dilution*) is not always the proper solution to this problem. Higher energy consumption, draught and expensive investments in building HVAC equipment and services could be the consequence. It has been estimated that almost half of the energy consumed in North America is used in buildings for lighting, cooling/heating and ventilation. Source control resulting in reduced emission and minimized ventilation requirements appears to be a more promising future strategy.

1.2 REVIEW OF PERTINENT LITERATURE

There are many sources of indoor air pollution, including emissions from building materials, furnishings and consumer products which emit pollutants, combustion (*as in the case of tobacco smoking or cooking and heating appliances*), and outdoor air. This review will focus on building materials and furnishings as the main source of VOC contaminants. A brief review of relevant parameters, which are commonly associated with the mass transfer phenomena, and research efforts reported in the literature, are presented in this section. The review is not intended to be extensive but rather to show clearly the conclusions of the previous researchers regarding the effect of environmental parameters on material emissions, the diversity of the test facilities used for testing the materials, and finally, the analytical methods used for analysing the emission data, with special focus on the major problems with the current source/sink models.

1.2.1 Basis for Determining Acceptable Indoor Air Quality

1.2.1.1 Volatile Organic Compound (VOC)

An organic compound having vapour pressure greater than 10^{-2} kpa at 25 °C is classified as a volatile organic compound. Also the boiling point sometimes is used as the criterion in which case, compounds with boiling points below 250 °C at the normal atmospheric conditions may be considered volatile organic compounds.

1.2.1.2 Acceptable Indoor Air Quality Criterion

According to the ASHRAE standard (1989) acceptable indoor air quality is “*air in which there are no known contaminants at harmful concentrations as determined by cognisant authorities and with which a substantial majority (80% or more) of the people exposed do not express dissatisfaction*”

1.2.2 Materials Affecting Indoor Air Quality

1.2.2.1 Solvents

The term solvent, whether as part of the chemical composition of the source or as a cleaning solution used to prepare the surface, simply means any material used to dissolve another material. The solvent can be water based (*aqueous system*) containing acids, alkalis, detergent and other materials as dissolving agents; or organic (*non-aqueous systems*) used to dissolve other organic materials. Organic solvents include materials such as naptha, mineral spirits, gasoline, etc. Hazardous volatiles, which are the focus of this thesis, frequently originate in organic solvents.

The ability of organic chemicals to cause adverse health effects varies greatly from those that are highly toxic, to those with no known health effect. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed. Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organic compounds. At present, not much is known about what health effects occur from the levels of organic compounds usually found in homes. Many organic compounds are known to cause cancer in animals; some such as benzene and methylene chloride are suspected of causing, or are known to cause, cancer in humans. Some other compounds are suspected of causing liver and kidney damage. Therefore, the physiological effects of various organic solvents is complex and variable, though certain generalizations can be made as follows:

- (i) The vapour pressure of organic solvents is usually high, which tend to result in high rates of volatile emissions. As a general rule, solvents have vapour pressures that will produce localized concentrations around 100 to 1000 parts per million (ppm), and even higher in the proximity of open pans even with good ventilation (Olishifski, J. and McElroy F. 1971).
- (ii) All organic solvents affect the central nervous system to some extent, acting as depressants and anaesthetics and cause other effects depending upon the degree of exposure and the volatile involved. These effects may range from mild unnoticed effects to insensibility (narcosis) and death from respiratory arrest.

(iii) When a solvent contacts or wets the skin it will tend to cause dermatitis or inflammation of the skin. This may take the form of simple irritation or more severely systemic damage to the skin. Even the most inert solvents will dissolve the natural protective barrier of fats and oils and leave the skin unprotected from further irritation and harm. The most common organic solvents can be classified as follow.

- Hydrocarbon- based

- Alcohol- based

- Glycol- based

- Ester- based

- Ketone- based

- Aldehyde-based

1.2.2.2 Dry Materials

Dry materials, which include the majority of materials used to construct and furnish residential and commercial environments, are characterized by relatively low emission rates of VOCs, which decay slowly. Such materials include wood products, floor coverings (*carpet, vinyl*), wall coverings (*wallpaper, fabric*), ceiling materials (*acoustic tiles, sub-floors*), and insulation (*fibreglass, rigid foam*). Heating, ventilating, and air conditioning (HVAC) components, such as duct liners also represent potential indoor air pollution sources. Furnishings, composed of pressed wood products and/or upholstery, are additional potential sources of undesirable VOCs.

1.2.2.3 Wet Materials

Modern construction techniques rely heavily on a wide variety of architectural coatings (*paints, stains, varnishes*), adhesives, caulks, and sealants. Such materials are applied “wet” and their initial emission rate (*mostly petroleum-based solvents*) are relatively high and decay rapidly.

1.2.3 Processes Affecting VOC Emissions

1.2.3.1 Sorption

The mass transfer to and from indoor sinks is primarily governed by adsorption and desorption processes. Adsorption and desorption are used to describe effects at the surface of a solid. In the case of adsorption, gas or vapour molecules are attached to a surface by physical or chemical means. Experimentally it is difficult to classify the characteristics of attraction as the adsorption may have a mixed physical and chemical characteristics (Flood, 1967). Several well-known adsorption isotherm theories have been developed to describe the adsorption/desorption behaviour of gas molecules with solid surfaces (*for example Langmuir, Freundlich, and Brunauer-Emmett*). IAQ researchers have begun to apply these theories to the behaviour of indoor sinks (De Bortoli et al. 1986 and Wallace et al. 1987).

1.2.3.2 Sink Effects

Indoor surfaces act as sinks by adsorbing the pollutant from the gas phase, and later when the concentration in the air decreases due to ventilation, the material will become an emitting source of the vapour phase organic pollutants as the deviation from equilibrium is

reversed. In this way the material behaves as a capacitor temporarily storing the contaminants and then re-emitting them, thereby delaying the expulsion of the volatiles from the building. Because of this, indoor sinks are believed to play a major role in determining the concentration versus time history associated with indoor sources, especially wet sources. Examples of indoor sinks include floors (*carpet, vinyl, rugs, plywood*), walls (*gypsum board, wallpaper, partitioning wall*), ceilings, HVAC system (*including supply and return air ducts and air filters*), and furnishings.

1.2.3.3 Diffusion

Diffusion plays a major role in source emission and sink interactions. After molecules are released from a source or sink by evaporation or desorption, diffusion through the boundary layer occurs. The compound's diffusion coefficient in air and the boundary layer flow characteristics control the rate of diffusion. In addition, the internal diffusion within the source or sink plays an important role in the emission from dry sources (*that is the molecule must be migrating by diffusion to the surface*).

1.2.4 Parameters Affecting Indoor Air Quality

Among the important environmental variables that impact material source emissions and sink behaviour are temperature, humidity, air change rate, and loading of materials, velocity, and turbulence. The impacts of these variables on material emissions are briefly reviewed in this section.

1.2.4.1 Temperature

The emission rate of volatile organic compounds (VOCs) from indoor materials and products is influenced by temperature. The three controlling processes for emissions: the internal diffusion within the material to the source surface, the surface desorption, and the evaporation from the surface, all increase with the temperature monotonically. Increased temperature may also accelerate chemical reactions within the material, leading to additional VOC emissions. Therefore, the temperature has a major impact on the material emission rate. Several studies describe *bake-out* of new or newly renovated buildings; by increasing the temperature, an attempt was made to increase the emission rate and thus achieve lower concentrations after a short *bake-out* period (Borazzo et al. 1993, Girman et al. 1989, and Offerman 1993). The success of *bake-out*, however, was inconsistent. The authors state that clear conclusions cannot be drawn because the concentration drop after the *bake-out* period was too small and could also have been caused by natural decay and/or change of ventilation conditions. All previous authors recommend that further research be under-taken, in particular systematic laboratory studies.

1.2.4.2 Humidity

Humidity has been shown to affect the emission rate of formaldehyde from pressed wood products and may have similar effects for other water soluble gases.

1.2.4.3 Air change Rate

Air change rate, expressed in air changes per hour (ACH), is defined as the volume of outdoor air that enters (*and leaves*) the indoor environment in one hour, divided by the

volume of the indoor space. The air change may occur by mechanical ventilation systems or by infiltration/exfiltration. The air change rate and loading ratio determines the amount of dilution and flushing that occurs in indoor environments. The higher the rate, the greater the dilution and the lower the indoor concentration of substances originating indoors. Thus, the air change rate can impact evaporative emission rates and the mass adsorbed on indoor sinks.

1.2.4.4 Velocity and Turbulence

In general, the higher the velocity and level of turbulence, the faster the mass transfer external to the solid. In a practical sense, above a certain velocity and level of turbulence, the resistance to mass transfer in the boundary layer is minimized (*that is, the mass transfer coefficient reaches its maximum value*) or the rate is controlled by effects other than those in the fluid boundary layer.

Before leaving this section it is worth mentioning here two important notes regarding the effect of the air velocity on the material emissions. First, in previous studies with wet materials being used as a source, the evaporative mass transfer mechanism is dominant. However, the conclusions may be completely reversed if the nature of the source is changed (*using dry source for example*) (Roache et al. 1994). Second, the surface air velocities inside these test chambers are not uniform and not precisely measured (*excluding Zhang et al. 1996*).

1.2.5 Sources Classification

From a modelling point of view, and for the purpose of this research, the sources of VOC's will be classified into two main groups.

(I) *Externally and internally controlled sources.*

These sources are characterised by high emission rates and fast decay rate in the initial period, followed by low emission rate and slow decay rate in the later period. They can be further classified as follows:

- Simple source (*evaporation or sublimation with no phase change in source*) for example, paint thinners, moth repellent...
- Complex source (*wet sources, which pass from external to internal control as the source dries*) for example, adhesives, caulks and sealants, latex paint, wood stain.

(II) *Internal diffusion controlled sources.*

These sources are likely to have emissions that persist over periods of weeks, months, and even years. Frequently a complex source begins the emission process under external mass transfer control, but shortly passes to internal diffusion control as the source dries and hardens. Also the internal diffusion controlled sources can be further classified as follows:

- Homogenous sources (*having uniform material properties*) such as vinyl flooring, carpet pad, treated wood

- Composite sources (*comprising an assemblage of homogeneous materials*)
for example, layered vinyl flooring, carpet with pile, plywood

1.2.6 Methods for Studying Emissions

A variety of methods are used by IAQ investigators to determine the chemical emissions from indoor materials and furnishings. Table 1.3 summarises the methods. The following discussion briefly describes the methods that are used at NRC, namely Dynamic Chamber Studies (*a complete description of the test facility used in this study is presented in Appendix-A*).

Table 1.3 Source Testing Methods

<u>FUNDAMENTAL COMPOSITION STUDIES</u>	
(1)	<i>Extraction and Direct Analysis</i> - provide information on material composition - do not provide emissions composition or emissions rate data
(2)	<i>Static Headspace</i>
<u>DYNAMIC CHAMBER STUDIES</u>	
(1)	<i>Small Chambers</i> - provide emissions composition and emissions rate data under controlled environmental conditions - chamber size may limit the use for some material sources (<i>for example, furniture, work stations</i>)
(2)	<i>Large Chambers</i> - provide emissions composition and emission rate data under controlled environmental conditions - large chambers may be required for evaluating emissions during the application phase of wet materials.
<u>FULL-SCALE STUDIES</u>	
(1)	<i>Test House</i>
(2)	<i>Field Studies</i>

1.2.6.1 Dynamic Chamber Studies.

In order to determine the impact of indoor sources on IAQ, information on the source emission rate is required. Such information can be obtained by dynamic, flow-through tests. Both sizes of chambers are available at NRC.

(a) Small Chambers

Small (0.4 m^3 and 0.05 m^3) environmental test chambers are used at NRC to evaluate emissions from indoor materials (Zhang et al. 1996). The small chamber facility includes a clean air delivery system, environmental controls (*temperature, humidity, airflow rate*), and sampling and analysis equipment. Emission testing is conducted by placing a sample in the chamber and measuring the concentration (*individual compounds or total organics "TVOC"*) at the chamber outlet. The sample size is usually determined by the "loading factor" (*that is, the ratio of the test specimen area to the chamber volume*). Concentration data are collected over a sufficient time interval to adequately describe the time history of the emission rate.

Small chambers have obvious limitations. Normally, only samples of larger materials (*for example, carpet*) can be tested. Small chambers may not be applicable for testing complete assemblages (*for example, furniture, work-stations*). For some materials, small chamber testing may provide only a portion of the emission profile of interest. For example, the rate of emissions resulting from the application of paints and coatings, by brushing or spraying, is higher than the rate during the subsequent drying process. Small

chamber testing cannot be used to evaluate the application phase of the coating process in a controlled environment.

(b) Large Scale Chambers

A large chamber (55 m³) is used to overcome the limitations of small chambers noted above (Zhang et al. 1994). As with small chamber testing, careful control of the environmental variables is necessary to ensure that accurate results obtained from large chambers are essentially the same as from small chambers, except in large chambers the sample is usually collected at one or more locations in the chamber instead of in the outlet flow.

1.2.6.2 Emissions Testing Costs

The cost of tests has discouraged nearly all but the largest product manufacturers from testing their products. These costs have ranged from \$1500 to \$3500 per test for individual products to more than \$10000 for complete workstations in environmental chambers (Levin et al. 1993 and Zhu, J. 1998). Concerns about product liability and possible misuse of the data have also been expressed by some manufacturers.

1.2.7 Using the Results of Source/Sink Evaluations

As discussed above, methods are available for determining the chemical emission rates of indoor sources and sink adsorption/desorption rates. This information is used in source and sink models to predict the emission rate as a function of time. The development of source and sink models relies heavily on experimental observations and understanding of the mechanisms. The rest of this chapter is devoted to the modelling efforts reported in the

literature. And for the convenience of discussion, we will divide all source and sink models into two main categories: *statistical models* and *mass transfer theory based models*. The major issues associated with the two kinds of models are highlighted in the next subsections.

1.2.8 Statistical Models

The most commonly used statistical model to approximate the emission rate data is the first order decay model (Zhang et al. 1996).

$$R(t) = R_0 e^{-kt} \quad (1.1)$$

The next step is to estimate the model parameters, namely the two coefficients R_0 and k that could give the best agreement between the model predictions and the experimental observation. Usually, data from small or full-scale chambers are used for estimating the model parameters. As one can see in this type of model, its development depends heavily on the curve fitting approach (*statistical estimation*).

Therefore, the statistical approach is easy and fast but it is associated with some severe problems. Some of these problems are:

- (i) Unlike the physical parameters (*such as boiling point, vapour pressure, diffusion coefficient, ..etc.*), the model parameters do not have distinct physical meaning,
- (ii) The model parameters are very sensitive to any change of the environmental conditions. This means that the parameters determined at a certain set of test

conditions (*e. g., air exchange rate and chamber loading factor*) do not apply at another set of environmental conditions.

- (iii) The model parameters vary with the ways used to fit the model to the chamber observations.
- (iv) Since it is based on a curve fitting approach, the models are often deficient in tracking the long-term emission that is beyond the test period.

1.2.9 Mass Transfer Theory Based Models

The second category is the mass transfer theory based models. To develop mass transfer theory based models, one needs to understand the physical-chemical phenomena involved, such as evaporation, adsorption, molecular diffusion through the air-surface interface, and molecular diffusion within the source. The parameters of a mass transfer model often have well-defined physical meanings such as vapour pressure, diffusivity, and boundary layer thickness. Therefore, parameter estimation for mass transfer models does not rely heavily on curve fitting (*statistical methods*).

Many mass transfer based models have been developed to describe the adsorption/desorption of VOC's by various indoor sinks/sources. (*Note that among the existing source and sink models, none are pure statistical models or pure mass transfer models*) Some include surface effects (Silberstein et al., 1988, Dunn and Tichenor, 1988, Tichenor et al., 1991, Clausen et al. 1991, and Chang and Guo, 1992), including an example where the boundary layer resistance between the bulk air and the source/sink was taken into account (Axley, 1991).

While other investigators have discussed the general mass transfer model for the evaporative mass transfer situation, Tichenor et al. (1993) proposed a model based on boundary layer theory, but they did not provide a means for scaling data from one environment to another. Gunnarsen (1991) discussed gas-phase-limited mass transfer for indoor sources with special emphasis on the effects of air velocities. He proposed correlations from the general mass transfer literature based on turbulent flow past spheres. Axley (1991) suggested that unidirectional flow over flat plates could be used to describe the emission from gas-phase-limited sources. Reiss et al. (1994) discuss the evaporative mass transfer sources and also suggest that the correlations developed for flow over flat plates could be used to predict the emission profile from indoor sources. Hansen (1974) studied the relative magnitudes of the mass transfer resistances for latex coatings and concluded that the internal resistance was larger than the boundary layer resistance. Feigley, et al. (1981) studied emission rates of solvents from surface coatings. They developed a mass transfer theory based model to analyze the results of their experiments but did not provide methods for generalizing their data.

Although all the researchers do agree that the emissions from indoor sources can be well described by mass transfer theory based models, none of the research in the literature gives a generalized model confirmed with experimental data.

The applicability of the existing physically based models is briefly considered in the light of experimental observations. Models that focus on surface effects appear inappropriate because many of the dominant compounds originate in the polymeric materials (*solid*) and seem to be subject to internal diffusion controlled release. The diffusion models of Dunn (Dunn, 1987; Dunn and Chan, 1992) assume an infinitely deep source, and cannot be used for finite sources that are significantly depleted. Clausen et al. (1992) considered a finite source, but used an empirical formula for the diffusion coefficient. Recently, Little et al. (1994) used a finite source, but used a statistical method for predicting the model parameters such as diffusivity " D ", initial concentration " C_0 ", and the equilibrium partition coefficient " k_p " (*multiple model parameters estimation with single least square regression*).

It should be pointed out that all the above diffusion models presumed that the only mass transfer mechanism is the diffusion through the source material, and hence, they neglect the influence of the vapour pressure of the emitted compounds in the surrounding air, or the gas film resistance to mass transfer (*i. e. they overlooked the boundary layer resistance*).

1.2.9.1 Special Problems with Mass Transfer Theory Based Models

In recent years, source and sink models based on basic mass transfer theories have received ever-increasing attention by the indoor air community (Little et al. 1994, and Tichenor et al. 1993). Many researchers, who have discovered the disadvantages of the statistical models, believe that fundamentally based models are the final solution to the

source sink modelling problems. In general, mass transfer models are preferred to statistical models because the former emphasizes the physical understanding of the real mechanisms and because their parameters are usually well defined. However existing fundamentally based models have three main problems.

(1) Introducing Some Adjusting Factors

To model very complex reality with relatively simple models, the modellers have to exclude whatever they consider "*unnecessary*" details and focus on one or two mechanisms. Due to the omission of the remaining mechanisms, the resulting models are often useless unless some adjusting factors are introduced. The following is an example of this problem. Guo et. al. (1996) tested the emissions of ethyl glycol, propylene glycol, and texanol from interior latex paint applied to a piece of gypsum board in a 5.3 L chamber (*0.5 air change per hour, 23 °C, and 50% relative humidity*). The ultimate goal of their work was to develop a source model that could predict the VOC emissions for both short (*evaporative controlled period*) and long term (*diffusion controlled period*) emission from latex paint applied to porous materials such as gypsum board. The resulting model is a combination of the first-order decay model (*which will account for the evaporative controlled period*) and an empirical diffusion model (*which will account for internal diffusion controlled period*). Their proposed model is outlined below;

$$R = M_0 k \text{Exp}(-kt) + \xi \left(\frac{0.632}{\phi} \right) M_D (D/t)^{0.5} \quad (1.2)$$

Where;

φ	Thickness of the source
ξ	Adjusting factor
k	Exponential decay constant
M_D	Mass available for diffusion

Despite the fact that, Eq. (1.2) has a sound physical basis, the introduction of the factor α (*they called it the adjusting factor*) makes it indistinguishable from the statistical one. Without this factor the model will give unrealistic emission results. These variables (*adjusting factors*) often make the mass transfer models less attractive because they have made the mass transfer models indistinguishable from empirical models.

(2) Estimating Multiple Parameters by Single Regression Analysis

All existing mass transfer based models have at least three parameters. Emission rates of VOC's from dry materials are primarily controlled by the diffusion within the material (*i.e., internal diffusion*) (Little et al. 1994). The diffusion process in its simplest form, may be described by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Where, D is the diffusion coefficient in the material;

C is the concentration in the material;

x is the spatial coordinate (assuming 1-D diffusion)

In order to apply the diffusion model for predicting the VOC's emission rates, it is necessary to know the diffusion coefficient, initial concentration, partition coefficient and/or convective mass transfer coefficient (*model parameters chapter V*) (Little et al. 1994, and Axley 1995). However, data on the diffusion and partition coefficients for building materials are very limited. Previous methods for determining the model parameters (*diffusion coefficient, partition coefficient, and mass transfer coefficient*) involved curve fitting of the diffusion model to the concentration data measured in a dynamic chamber test for VOC's emissions (Little et al. 1994 and Zhang et al 1996). These methods require that multiple parameters be estimated in a single least-square regression analysis, and thus may result in large estimation error due to inter-dependency of the parameters in the regression analysis process. As can be seen later, the main focus of the present work is to develop a new experimental method for independent determination of the model parameters more precisely without resorting to the curve-fitting procedure. In general, mass transfer theory based models are often much more complicated than their corresponding statistical models.

(3) Neglecting the Sink effect

The interaction of indoor air pollutants with interior surfaces (*i.e., sink*) is a well-known, but poorly understood phenomenon. It is also known that adsorption and desorption processes can affect the dispersal of contaminants in buildings. The evidence is pervasive. Tichenor et al. (1988) reported on studies in an IAQ test house where para-dichlorobenzene was measured in significant concentrations several days after the source (*moth repellent*) was removed. Measurements in the same test house, taken 12 months after previous moth

repellent emission tests, showed concentrations of para-dichlorobenzene well above the outdoor concentration, indicating the re-emission of the para-dichlorobenzene previously adsorbed on interior surfaces. The same authors reported that organic compounds adsorbed on building materials in a 7-year old pre-school were re-emitted when placed in a small environmental test chamber ventilated with clean air. The evidence of sink effects can also be noted in our daily life. For instance, the lingering odours of winter clothes stored during

the summer with naphthalene crystals, and the odour of clothes exposed to tobacco smoke or gasoline fumes that persists for days or until washed are but two examples.

Despite the importance of the sink effects on materials emission studies, the interaction between the vapour phase organic compounds and the indoor sinks are generally overlooked. Very few mass transfer theory based models incorporating the sink effect with the sources are reported in the literature. The reason is that, the majority of the emission tests used to validate the source models are conducted in the small or full-scale chambers, where the walls and the connections that may come in contact with the gas phase are made of electro-polished stainless steel. This ideal test environment (*Artificial envelope*) underweighted the importance of the sink effect and the model predictions compare well with the chamber data. However, if the model predictions are compared with the experimental data conducted in the real case scenario (*For example, data from the test house*), the model will

over estimate the concentrations in the early time and under estimate the concentrations in the long term. This model deficiency I believe may be attributed to the sink effect (*Excluding the sink effect*). Furthermore, even stainless steel chambers showed a considerable amount of sink effect for high boiling point compounds (Tichenor et al. 1991, Chang and Sparks 1997 and An et al. 1998) which should be accounted for in emission testing.

The following is an example for the sink strength of different indoor materials including the electro-polished stainless steel chamber. In a comprehensive study aimed at characterising the sink strength of different indoor materials/furniture, An et. al (1998) designed an experiment to evaluate the sink strength of aged carpet, vinyl flooring, gypsum board and ceiling tile. Each material was tested with five organic compounds *{the boiling point of the five VOCs ranged from 136 °C (ethyl-benzene) to 216 °C (dodecane)}*. A specimen holder was used to control the surface area, and the edges of the materials were sealed with wax. The tests were conducted in a 50 l environmental test chamber. The test chamber was made of specially treated stainless steel (*electro-polished*). The standard test conditions were: (1) Air exchange rate 0.5 hr^{-1} (2) Temperature $23 \text{ }^{\circ}\text{C}$ (3) Inlet air relative humidity 50% (4) Chamber loading factor $0.57 \text{ m}^2/\text{m}^3$. The sample was placed in the test chamber supplied with clean air. At the start of each test, a portion of the inlet flow was replaced by flow from a constant temperature oven that held a permeation tube containing the test compound (*we refer to this stage as dosing/adsorption phase*). The concentration of the compound was

monitored at both inlet and outlet of the test chamber. The sink strength of the material was characterised by the difference between the inlet and outlet concentrations. Once the chamber concentration reached an apparent equilibrium value (*usually after about one-week*), the flow from the permeation oven was shut off and replaced by flow from the clean air cylinder (*we refer to this stage as purging/desorption phase*).

To characterise the sink strength, a model based on a first order reversible surface adsorption/desorption phenomenon was suggested. Assuming a perfectly mixed small test chamber, the governing equations for chamber concentration are:

$$\frac{dC}{dt} = Lk_a M_{so} - (Lk_a + N)C + NC_{in} \quad (1.3)$$

$$\frac{dM_{so}}{dt} = -k_d M_{so} + k_a C \quad (1.4)$$

Where:

k_a is the adsorption rate constant, m/hr

k_d is the desorption rate constant, $1/hr$

M_{so} is the mass in the sink per unit surface area, mg/m^2

The solutions of the above equation during the adsorption and desorption phases are given below;

$$C_a = C_m \left\{ 1.0 - \frac{(N + r_1)e^{-r_1 t} - (N + r_2)e^{-r_2 t}}{r_2 - r_1} \right\} \quad (1.5)$$

And

$$C_d = \frac{[Lk_a M_{ad0} - (N + Lk_a + r_2)C_m]e^{-r_2 t} - [Lk_a M_{ad0} - (N + Lk_a + r_1)C_m]e^{-r_1 t}}{r_2 - r_1} \quad (1.6)$$

Where:

C_m is the concentration introduced to the test chamber, mg/m^3

r_1, r_2 are the two parameters estimated by Eq. (1.9)

On the other hand, if there was no sink effect and the chamber air was well mixed, a mass balance indicates that, the VOC's concentration in the adsorption phase C_a should approach the value of C_m in a fashion as;

$$C_a = C_m [1.0 - \text{Exp}(-Nt)] \quad (1.7)$$

Whereas, the VOC's concentration in the desorption phase C_d should decrease exponentially;

$$C_d = C_m \text{Exp}(-Nt) \quad (1.8)$$

$$r_{1,2} = \frac{N + Lk_a + k_d \pm \sqrt{(N + Lk_a + k_d)^2 - 4Nk_d}}{2} \quad (1.9)$$

Table 1.4 Adsorption/desorption coefficients of three materials with two VOCs (An et al. 1998)

<i>Compound Name</i>	<i>Ethyl-benzene</i>	<i>Dodecane</i>
Empty Stainless Steel Chamber		
k_a (m/hr)	0.143±0.077	0.0168±0.0013
k_d (hr ⁻¹)	23.3±120	0.0935±0.011
k_s (m) ($k_s = k_d/k_a$)	0.00613	0.179
Painted Drywall		
k_a (m/hr)	0.0878±0.087	0.129±0.0095
k_d (hr ⁻¹)	1.196±1.2	0.0397±0.0053
k_s (m)	0.0734	3.27
Carpet		
k_a (m/hr)	0.534±0.16	0.492±0.021
k_d (hr ⁻¹)	0.462±0.17	0.0247±0.0015
k_s (m)	1.158	19.9

Equations (1.5), (1.6), and (1.7) were used to analyse the chamber data, and the values of sink parameters, k_a and k_d were estimated by a non-linear regression curve fit routine. As illustrated by Figure 1.1 the sink effects during the adsorption and desorption phases are described by the differences between the concentrations predicted by Equations (1.7 and 1.8) and the chamber data. In Figure 1.1 (*the empty chamber with dodecane*) the chamber concentrations were considerably lower than that predicted by Eq. (1.7) during the adsorption phase, and higher than that predicted by Eq. (1.8) during the desorption phase. This trend indicates that, the empty chamber walls behave as a capacitor during the adsorption phase (*temporarily storing the contaminants*), and then re-emitting them, thereby increasing the chamber concentrations during the desorption phase. The question that arises now is, if this is the case with an empty stainless steel chamber, then what do we expect by way of the sink effects in a real house, where the sink capacity k_s of the

interior surfaces are at least two orders of magnitude higher than the stainless steel? (See the value of k_c in table 1.4). And more importantly what are the consequences of neglecting the sink effects when validating any model? Since the source models are seldom used alone, and they are usually used in an IAQ model, any predictive errors that the sink effect generates can be propagated to the IAQ simulation results.

Figure 1.1 Adsorption/Desorption of Dodecane in an Empty Chamber

The following example will answer part of the above question. In the experiment described by J. Chang et al. (1994), 6 m² of oak flooring was stained in a test house having a volume of 305 m³. As Figure 1.2 illustrates, the model prediction in the absence of re-emissions from sinks shows that the concentration would be reduced to background in less than 50 h. However, the actual test data and the predictions of the model

incorporating the sink effects show that the concentrations exceeded background level for at least 500 hr.

Figure 1.2 Comparison of Test House Nonane Data with Predictions of IAQ Model

(Reproduced from J. Chang et al. 1994)

Many other investigators have also given an overview of the significance of the sink effect in the stainless steel chambers. For example, Neretnieks et al. (1993) and recently Little et al. (1995), concluded their papers by emphasising the need to incorporate the sink effect in future work.

1.2.10 Conclusions Based on the Literature Review

The prominent effect of surface air movement, relative humidity, and temperature on material emissions, as well as the methods of studying emission, and using the results of source/sink evaluations, have been briefly reviewed in this chapter. Almost all the previous workers stated the same conclusion regarding the effect of some environmental parameters on the material emissions (*namely, the effect of temperature, relative humidity, and air exchange rate*). However, the complexity of the material emissions problem and the difficulty and lack of conformity in experimental procedures impede the clear cut conclusion regarding the effect of the surface velocity, though certain generalization can be made:

- (1) When the emission is controlled by evaporative mass transfer mechanism (*as is the case of wet sources*), the external parameters such as air velocity, the level of turbulence and air exchange rate, play an important role in determining the material emissions rate.
- (2) On the other hand, when the internal diffusion within the material is the controlling mass transfer mechanism (*as is the case of dry sources*), the velocity, turbulence intensity, and the air exchange rate have very little effect (*if any at all*) on the material emissions.
- (3) The wet source such as latex paints, wood stain, caulks and sealant begin the emissions process under external mass-transfer control, but shortly pass to internal diffusion control as the source dries and hardens. This emphasises the significance of the internal diffusion process as a dominant mechanism even in the case of wet sources.

- (4) Most of the existing test chambers are built with environmental controls such as temperature, humidity, and ventilation rate controls. They generally have well-mixed air inside, however, the air velocities inside these test chambers are not uniform and not precisely measured. Thus, it is difficult to use them for studying the effect of surface air movement on emissions from wet sources.
- (5) Many researchers, who have been frustrated by elusive statistical models, believe that fundamentally based models are the final solution to the source sink models problems. Strong evidences from previous workers supports the notion that VOC emissions from dry building materials/products are governed by well-established mass transfer principles and hence are predictable using mass transfer based models. In general, mass transfer models are preferred to statistical models because the former emphasise the physical understanding of the real mechanisms and because their parameters are usually well defined. It is generally true that a mass transfer model has better "validity" than a statistical model.
- (6) Previous methods for determining the model parameters (*diffusion coefficient, initial concentration, partition coefficient, and/or mass transfer coefficient*) involved curve-fitting of the diffusion model to the concentration data measured in a dynamic chamber test for VOC's emissions (Little et al. 1994, and Zhang et al. 1996). These methods require that multiple parameters be estimated in a single least-square regression analysis, and thus may result in large estimation error due to inter-dependency of the parameters in the regression analysis process.

- (7) Although, system assembly (*substrate // glue // carpet* or *substrate // glue // vinyl tile*) is commonly used in residential and commercial buildings, the modelling efforts for material systems are very limited.
- (8) Indoor sinks can dramatically extend the time of elevated concentrations due to source emissions. Excluding the interaction between the vapour phase organic compounds and the indoor sinks (*the sink effects*) will result in the predictive errors during an IAQ simulation especially for high boiling point compounds.
- (9) Perhaps the most important conclusion that can be drawn from the literature review regarding the emission from the dry sources is that under typical environmental conditions, the behaviour of a source that is controlled by internal diffusion is largely independent of the chamber. So the prediction of the diffusion controlled source/sink behaviour of indoor materials may possibly be based only on a knowledge of the pre-determined properties of the relevant VOC and the indoor material.

1.3 SCOPE AND SIGNIFICANCE OF PRESENT WORK

With the growing awareness of the problems associated with indoor air quality, there is now a strong impetus for manufacturers to produce, and for architects and designers to select, lower emitting building materials. Success in both manufacturing and choosing environmentally-conscious building materials will be greatly facilitated by truly understanding the physical-chemical phenomena involved, such as adsorption, evaporation, and molecular diffusion within the boundary layer, and molecular diffusion within the

source. Such knowledge can help identify and understand the more toxic or irritating sources, and suggest ways to reformulate building materials to reduce emissions without incurring any significant loss in performance.

The Institute for Research in Construction (*IRC*) at the National Research Council of Canada (*NRC*), is currently conducting a comprehensive research project on material emissions and IAQ modelling (launched in 1995) that is aimed at achieving a coherent understanding of the fundamental mass transfer mechanisms governing the emission from a wide range of building materials/products. The end goal of the material emissions project include (Zhang and Shaw 1996): (i) developing procedures and methods for testing material emissions (ii) developing a database of measured emission characteristics for various building materials and furnishings, and finally, (iii) developing integrated computer software for predicting the concentration of contaminants in buildings.

This thesis is part of a collaborative research program between the Department of Mechanical and Aerospace Engineering at Carleton University, and the Institute for Research in Construction at the National Research Council of Canada. So within the main frame of the material emission project, the objectives and significance of this thesis were;

- (1) To develop and validate a mass transfer theory based model to predict the emission rates from *dry sources* as a function of time and environmental parameters.
- (2) To develop a method and experimental procedure for simultaneous measurements of diffusion and partition coefficients of different compounds through solid materials (*such as*

carpet, plywood, vinyl floor, plywood,etc). (Equilibrium partition coefficients is a coefficient used to describe the relationship between the concentration in the gas phase and the concentration in the solid phase).

(3) To develop a mathematical model to predict the diffusion coefficient through complex sources as a function of time (*Note that, complex sources pass from external control to internal diffusion control as the source dries*). And to use this model (*for diffusion coefficient in complex sources*) to predict the emission rate from a material system (*namely, substrate // glue // vinyl tile*).

The uniqueness of the new modelling approach is that:

- (i)* All the model parameters have well defined physical meanings (*either physical properties of the source or the environment*).
- (ii)* It characterise a diffusion-controlled homogeneous source *by independently measuring the model parameters (such as D , k_e , h , C_0) and comparing predicted emissions to experimental chamber observations*, so that the estimation error due to inter-dependency of the model parameters in the regression process will be eliminated. The role of the partition coefficient is developed in chapter III.
- (iii)* The model parameters are measured directly for each component without resorting to dynamic chamber testing which will substantially reduce the need for standard chamber studies when investigating diffusion controlled sources.
- (iii)* It will extend the homogeneous source characterisation methodology to a composite source comprising an assemblage of homogeneous components.

(iv) It separates the properties of environment (*for example* N, Q, V) from those of the source (*for example* $C_0, D, L, \dots$ etc), so that the impact of each parameter on the emissions from the dry sources can be investigated. This will greatly facilitate product reformulation strategies aimed at preventing pollution by developing a clear understanding of the factors that control the emission process.

(v) The interaction between the vapour phase organic compounds and the sink surfaces (*sink effects*) will be included in this model.

The experimental measurement of the diffusivity of VOC's in the system components (*Resistances*) from the materials tested in this study as well as the result in (1) will contribute to the development of the data base of VOC's emissions from the building materials/products. These results will be very useful for designers and building owners to specify building materials/products to meet given exposure limits of VOC's concentrations.

Ventilation engineers can also use the results to estimate the impact of changing ventilation system operating conditions or building furnishings on the contaminant concentrations in their buildings. Since, validating a model is as important as creating one, and can be an original contribution to science, for this reason, the validation procedure will include:

- (i) Checking the agreement between the model prediction and a single set of observations from the small-scale chamber (*validating the modelling approach with emission data from two dry sources namely sub-floor tile and particle board*);

- (ii) Checking the agreement between the model prediction and a single set of observations from the full-scale chamber (*validating the modelling approach with emission data from material system assembly namely, 1/4" plywood // sub-floor tile // 5/8" plywood*).

Finally, this research represents the first coherent attempt to characterise diffusion-controlled sources by independently measuring the model parameters, and comparing the predicted emissions to experimental chamber observations. This modelling approach will eliminate the need for standard chamber studies, at least when investigating the diffusion controlled sources. Also it will provide a sound theoretical foundation for the characterisation of homogeneous, composite and complex source behaviour. Although specific sources were evaluated in this study, the approach and the results will have broad applicability to most building materials/products that release VOC's into the indoor environment.

1.4 HOW THIS THESIS IS ORGANISED

As stated earlier, this work is aimed at characterizing diffusion controlled sources by independently measuring the model parameters (*model parameters are determined without the use of a chamber emission data*) and comparing predicted emission to experimental chamber observations. Therefore, this study was divided into four main phases. The first phase of this research therefore consisted of a brief study aimed at identifying the most abundant volatile compounds in each product (*GC/MS screening phase*). Based on the results of this phase (*GC/MS screening phase*) specific volatile

organic compounds (VOC's) were targeted for testing in the second and third phases. In the second phase the test facility (*Diffusiometric apparatus*) was developed and used to determine the diffusion and partition coefficients (D and k_p) of the selected species through each individual material. In the third phase, the small- scale chamber was used to generate a set of emission data for some product tested in the first phase. As previously stated, verification of scale-up methods requires data from either real buildings or large test chambers. Without this step, the usefulness of a model cannot be justified. Consequently, in the fourth phase a full-scale chamber was used to generate a second set of emission data for model validation. Finally, the observed data (*small and full- scale chamber*) is compared with the predicted data (*model prediction*). Comparing emission data predicted by using independently measured model parameters to those observed in an experimental chamber serves as an exceptionally rigorous test of the validity of the current modelling approach. Therefore, due to the dependent nature of the thesis phases on each other, and for convenience of discussions, this thesis was organized so that each phase is presented in a separate chapter. For instance, all the materials of phase one (*The headspace studies*) including the test procedure, and the results and discussions of the headspace studies are documented in the second chapter (**Chapter II**). The materials of the second phase (*measurements of the diffusion and partition coefficients*) including the test facility used, the theory, the test procedure for measuring the diffusion coefficient, and the results and discussions are documented in the third chapter (**Chapter III**). The procedures used to characterizing the emission of the test materials, and the results of the measurement of VOC emission using the dynamic environmental chambers are

documented in the fourth chapter (**Chapter IV**). Finally, the developments of the mass transfer based prediction models for dry and complex sources, and the results of the experimental validations of the prediction models (*second and third phase*) are documented in the fifth and sixth chapters of this thesis (**Chapters V and VI respectively**).

It should be pointed out that, although each phase of this study was documented in a separate chapter, the thesis materials are still linked together via the output of each chapter. For instance, the equilibrium headspace concentrations C_{bag} (*generated from chapter-II*) were used: **(1)** to estimate the proper air sample volumes for subsequent dynamic chamber testing (*described in Chapter-IV*); this volume must be precisely calculated in order to avoid under or over-loading the GC/FID column, **(2)** the equilibrium headspace concentration C_{bag} was used to calculate the initial concentration in the specimen ($C_0 = k_c C_{bag}$). The initial concentration C_0 is a very important input parameter in the modelling process (*In Chapter-V*). Similarly, the results of chapter III (*diffusion and partition coefficients*) were used in chapters V and VI as the model input parameters. The following flowchart summarizes how this thesis is organized.

Figure 1.3 Flowchart of the thesis outline

Chapter II

HEADSPACE ANALYSIS

2.1 INTRODUCTION

This chapter deals only with the headspace analysis. For the convenience of discussion, it is divided into three main sections. The first section is devoted to describing the test plan, and the test materials. In the second section (*section 2.3*) the test procedure used for conducting the headspace analyses is described. In the third section, the results of the headspace studies are discussed and some conclusions made based on the headspace analyses results. Based on the results of the headspace analyses, specific VOCs were selected for testing in the subsequent phases of the study (*chapter III, IV, and VI*). Results from the headspace analyses also provide the equilibrium headspace concentration C_{bag} which is needed for: (i) estimating the proper air sample volumes for subsequent dynamic tests (*this volume must be calculated in order to avoid under or over loading the GC/FID column*) (ii) calculating the initial concentration in the specimen ($C_0 = k_r C_{bag}$). The initial concentration C_0 is a very important parameter in the modelling process (Chapter IV).

2.2 TEST MATERIALS

Test materials included in this study were particleboard, oriented strand board (*OSB*), plywood, gypsum board, sub-floor tiles (*Recycled automobile tires*), and vinyl flooring. These materials were obtained from their respective manufacturers or local retailers. All these materials are considered “*Dry*” products. The first three are known as the engineered wood products. Each dry product was stored in a tedlar bag from the time it was manufactured until the time it was used for a test. In preparation for testing, the materials were cut into the desired dimensions, and stored back in their bags in an environmentally controlled room with a clean air supply. Air conditions were maintained at 23 ± 1 °C and $50\% \pm 5\%$ RH. This allowed VOCs in the specimens to reach the equilibrium condition and the test materials to be in equilibrium with the test condition. The detailed specifications of each product including the manufacturer’s name will be given in the next subsections.

2.2.1 Particleboard

Particleboard is a panel product made of wood particles bonded together under heat and pressure, usually using a ureaformaldehyde resin adhesive, which produces a water-resistant, but not water-proof bond. It is layered with the finer particles in the surface layers and coarser particles in the core layer. The table below gives more detailed information about this material.

Table 2.1 Particleboard Specifications

Material:	Particleboard, 5/8" Industrial
Obtained from:	GP Flakeboard, Bancroft
Production Date:	12-Nov-97
Date Received:	17-Nov-97
Storage Conditions:	Tedlar bag, (Standard cond.)

Specimen dimension, Uncut (m)	Length	0.45
	Width	0.212
	Thickness	0.016
Specimen dimension, cut (m)	Length	0.212
	Width	0.212
	Thickness	0.016

Specimen Mass:	Date	Mass (g)
(a) Before Test	1-Dec-97	489.58
(b) After Test	6-Feb-98	497.30
Specimen Volume (m³)	Cut	0.00071
Specimen Density (kg/m³)	Cut	685.1
Specimen Surface Area	With Sample Holder	With-out Holder
(a) Top	0.0342	0.0449
(b) Bottom	0.0	0.0449
(c) Edges	0.0	0.0135
(d) Total Area	0.0342	0.1033

2.2.2 Plywood

Plywood is a panel consisting of thin veneers (*plies*) glued together so that the grain direction of each ply is perpendicular to that of the adjacent ply and symmetrical about the central ply or panel centerline. This cross-lamination provides two-way strength and stiffness properties, and good dimensional stability. Many kinds of plywood are manufactured in Canada. The product chosen for testing belongs to the *GIS (Good One*

Side) group (i.e., "Sanded, best appearance one side only, and may contain neat wood patches, inlays or synthetic patching material"). This kind of plywood is used where the appearance on one side is important such as in the case of furniture, cabinet doors, partitions, shelving, and concrete formwork.

Table 2.2 Plywood Specifications

Material:	GIS plywood 5/8" Industrial	
Obtained from:	Canadian Plywood Association	
Production Date:	25-Feb-98	
Date Received:	10-Mar-98	
Storage Conditions:	Tedlar bag, (Standard cond.)	

Specimen dimension, Uncut (m)	Length	0.5
	Width	0.3
	Thickness	0.016
Specimen dimension, cut (m)	Length	0.212
	Width	0.212
	Thickness	0.016

Specimen Mass:		Mass (g)
(a) Before Test		450.69
(b) After Test		459.13
Specimen Volume (m³)	Cut	0.00071
Specimen Density (kg/m³)	Cut	634.77

2.2.3 Gypsum board

The gypsum board tested is a SHEETROCK brand Gypsum Panel, FIRECODE Core type. It is composed of a fire-resistant core encased in a heavy natural-finish paper on the face side suitable for paint, wallpaper and other decoration, and a strong liner paper on the backside. According to the manufacturer, this composition provides a number of

performance benefits, including quick installation and decoration, fire protection and resistance against cracking and warping.

Table 2.3 Gypsum board Specifications

Material:	5/8" Sheetrock Firecode Core Type X		
Obtained from:	Hagersville #2 Line		
Production Date:	27-Feb-98		
Date Received:	3-Mar-98		
Storage Conditions:	Tedlar bag, (Standard cond.)		

Specimen dimension, Uncut (m)	Length	0.45
	Width	0.25
	Thickness	0.016
Specimen dimension, cut (m)	Length	0.212
	Width	0.212
	Thickness	0.016

Specimen Mass:	Mass (g)	
(a) Before Test	478.31	
(b) After Test	459.58	
Specimen Volume (m³)	Cut	0.00071
Specimen Density (kg/m³)	Cut	669.3

2.2.4 Oriented Strand Board (OSB)

This product belongs to the engineered wood class. The specifications and some other important information are summarized in table 2.4 below.

Table 2.4 OSB Specifications

Material:	OSB (aspen poplar); 7/16"
Obtained from:	Norbord Val d' Or
Production Date:	07-Mar-98
Date Received:	13-Mar-98
Storage Conditions:	Tedlar bag, (Standard cond.)

<i>Specimen dimension, Uncut (m)</i>	Length	0.45
	Width	0.25
	Thickness	0.0159
<i>Specimen dimension, cut (m)</i>	Length	0.212
	Width	0.212
	Thickness	0.0159

<i>Specimen Mass:</i>		<i>Mass (g)</i>
		178.82
<i>Specimen Volume (m³)</i>	<i>Cut</i>	0.00026
<i>Specimen Density (kg/m³)</i>	<i>Cut</i>	687.77

2.2.5 Sub-floor Tile (Recycled Automobile Tires)

Recently, a new substance has been introduced to the market as a building material, the main component of which is recycled automobile tires. The automobile tires are treated chemically (*Recycled*), melted and cast again in the form of sheets with different dimensions ($1.5 \times 1.8 \text{ m}$). These sheets are used indoors as a part of the floors to absorb sounds and vibrations. Although, this material may function well from a sound and vibration point of view, it may have a negative impact on the indoor air quality (*it may be a source of volatile organic compounds VOCs*). Therefore the impact of using this material as a part of floor on the indoor air quality is the main interest in this study.

Table 2.5 Sub-floor Tile Specifications

Material	Sub-floor Tile (Recycled Automobile Tires)
Obtained from	Royal Mat, Inc
Production Date	26-Jan-98
Date Received	20-Feb-98
Storage Conditions	Tedlar bag, (Standard cond.)

Specimen dimension, Uncut (m)	Length	0.45
	Width	0.25
	Thickness	0.016
Specimen dimension, cut (m)	Length	0.212
	Width	0.212
	Thickness	0.016

Specimen Mass:		Mass (g)
(a) Before Test		478.31
(b) After Test		459.58
Specimen Volume (m³)	Cut	0.00071
Specimen Density (kg/m³)	Cut	669.3
Specimen Surface Area	With Sample Holder	With-out Holder
(c) Top	0.0342	0.0449
(f) Bottom	0.0	0.0449
(g) Edges	0.0	0.0135
(h) Total Area	0.0342	0.1033

2.2.6 Vinyl Floor Tile

The vinyl floor tile tested in this study was a vinyl-based tile. It was obtained from a local retailer.

Table 2.6 Vinyl floor Tile Specifications

Material:	Vinyl flooring tile
Obtained from:	local retailer
Storage Conditions:	Tedlar bag, (Standard cond.)

<i>Specimen dimension, Uncut (m)</i>		Length	0.305
		Width	0.305
		Thickness	0.003
<i>Specimen dimension, cut (m)</i>		Length	0.17
		Width	0.17
		Thickness	0.003

<i>Specimen Mass:</i>		<i>Mass (g)</i>	
(a) Before Test			194.86
(b) After Test			194.54
<i>Specimen Volume (m3)</i>	<i>Cut</i>		0.0000867
<i>Specimen Density (kg/m3)</i>	<i>Cut</i>		2247.52

2.3 TEST METHOD AND PROCEDURE (GC/MS SCREENING)

The initial stage of this work consisted of a brief study aimed at identifying the most abundant volatile organic compounds in each product. In the absence of any sources of information such as product labels, or/and safety data sheets, headspace analysis remains the only reliable sources of information. Even though some data from the manufacturers are available, it is evident that the product is undergoing chemical changes during the shelf life. Because of these changes the compounds that are given off may differ from those in the original product formulation (*stated in the product label*). Therefore, it is important to conduct identification tests on the test materials prior to any emission study. This section will describe the test method and procedures used in this study to conduct the headspace analysis. The first section will describe the headspace test procedure for the floor adhesive. And the second section describes the test procedure for dry sources.

2.3.1 Headspace Analysis for the Floor Adhesive

As stated above, previous studies have indicated the potential of building materials in contributing to poor indoor air quality by emission of volatile organic compounds. Many of these studies identified floor adhesives as particularly important sources of VOCs in indoor air (Low 1996, Li, 1997, and Black et al. 1991). Adhesives are also suspected of causing widespread health complaints in at least one office building (Brown-Skeers, 1984). The emission of VOCs from the most commonly used type of adhesives were investigated in this study. The adhesive was selected for study based upon a broad range of applications and is formulated for bonding of carpets, vinyl floor tiles, and sub-floor assemblies (*Multi-purposes adhesive*).

A sufficient quantity of *Roberts 900* adhesive was purchased for the test. The purchased adhesive was mixed and then divided into 150 *ml* glass vials (*10 vials*) and sealed with Teflon-faced septa (*Each vial was used for only one test*). Then after about 7 days, a gas-tight syringe was inserted through the septum of one of these vials, and approximately 0.5 *ml* of the headspace gas was withdrawn. This gas sample was injected through a zero air supply onto a sorbent tube (*see Figure 2.1*) which was then analyzed using the thermal desorption *GC/MS* system. During the course of the evaluation, the volatile organic compounds that are found in the headspace of the product are used to select a gas chromatographic (*GC*) column, and to develop a set of operating conditions (*separation method*) that will permit the rapid and reliable separation of these compounds during the chamber emission testing. The separation of the compounds is optimized, and the major peaks in the chromatogram are interpreted with the aid of computer searching, then the

retention time of the mass spectra of known compounds available in the computer library (*Database*) are matched by retention time of the adhesive's headspace gases. Furthermore, the identification made by computer searching was confirmed by pure compounds spiking. It should be pointed out that the headspace analysis results from the adhesive at different sampling times (48, 72, 120, and 192 hours) shows the same chromatograms (*the same peaks*). This implies that there are no chemical reactions involved in this type of adhesive during the application or curing phase. This conclusion was confirmed by private communication with the adhesive's manufacturer (Zhu J. 1998).

Figure 2.1 Syringe Sampling Set-up

2.3.2 Headspace Analysis for the Dry Materials

In the dry materials headspace studies, both the ASTM static chamber and the tedlar bags were used following standard ASTM headspace procedures. The ASTM static chamber is a 50 l air tight stainless steel container equipped with two sampling ports as shown in Figure 2.3. The material under study was cut to the desired dimension and placed in the

chamber. Then after about 7 days, headspace samples were taken from the sampling port to determine the main volatile organic compounds in each product. Identification of the compounds was done on the HP MSD 5890/5970 GC/MS using a 60 m, 0.25 ID DB-5 type capillary column with temperature programs which vary from product to product. Triplicate headspace samples in each test were taken by slowly pumping air from the ASTM chamber through a three-layered sorbent tube. It should be pointed out that, prior to any test the ASTM static chamber was flushed with clean air from the standard air cylinder for more than 24 hr. And in order to detect and minimize any cross-contamination of the headspace chamber during specimen loading, air samples were taken from both the ASTM chamber outlet and the laboratory space immediately before the material was placed in the ASTM static chamber. The Step by step procedure used for conducting the headspace analysis for the dry sources is summarized below.

- (1) The headspace chamber was cleaned thoroughly with laboratory detergent and distilled water
- (2) Then Methyl-Alcohol (*Methanol*) was used to clean the inner surfaces of the test chamber, giving strict attention to the seams within the test chamber.
- (3) The test chamber was then closed and flushed by ultra zero compressed air for about 4 hours.
- (4) After 24 hours, an air sample was drawn from the headspace test chamber to check the background contamination level.
- (5) The tube was removed and analyzed by gas chromatography (*GC/FID*) to determine if there was any residual contamination of the test chamber. If there was evidence of

- (6) significant residual contamination of the headspace chamber, the procedure was stopped and chamber re-cleaned or flushed until the contamination had been reduced to an insignificant level.
- (7) After the background level had been confirmed, the test material was cut to the desired dimension and placed in the *ASTM* headspace chamber (*or the tedlar bag*). The chamber was closed and left at the laboratory environment condition. In order to detect and minimize any cross-contamination of the headspace chamber during specimen loading, air samples were taken from the laboratory space immediately before the material was placed in the *ASTM* headspace chamber.
- (8) After 7 days air samples of the headspace gas were slowly pumped from the *ASTM* chamber through three layered sorbent tubes (*usually triplicate samples were taken with each of different sample volume*). The air samples were analyzed by using the GC/MS. The tubes were analysis in the order of low to high sampling volume to avoid possible over loading of the analytical system.
- (9) The GC peaks were identified by comparing with those in the standard mass spectrum library. The identification of each selected *VOC* was confirmed by spiking with a corresponding *VOC* standard (*the retention time of known spiking compounds and unknown peaks are compared for positive identifications*)
- (10) The equilibrium concentrations C_{bag} of selected *VOCs* of interest were quantified and recorded. It should be pointed out that the equilibrium concentrations C_{bag} quantified in this phase were used later in the third phase for determination of the

initial concentrations in the source C_0 ($C_0 = k_e * C_{bag}$). Table 2.7 summarizes the test conditions of headspace analysis for each material tested.

Table 2.7 Test Materials Screening Analysis Test Plan

Material	Equilibrium Time (hr)	Volume taken (ml)	Facility used	Separation Method (Temp. Program)	Supplier
<i>Particle board</i>	<i>160</i>	<i>300</i>	<i>ASTM chamber</i>	<i>50-240^oC</i>	<i>Manufacturer</i>
<i>Sub-floor (Recycled Automobile Tires)</i>	<i>120</i>	<i>300</i>	<i>ASTM chamber</i>	<i>50-250^oC</i>	<i>Manufacturer</i>
<i>Gypsum board</i>	<i>160</i>	<i>10000</i>	<i>ASTM chamber</i>	<i>50-240^oC</i>	<i>Manufacturer</i>
<i>Carpet</i>	<i>160</i>	<i>300</i>	<i>ASTM chamber</i>	<i>50-250^oC</i>	<i>Manufacturer</i>
<i>Vinyl Floor Tiles</i>	<i>120</i>	<i>500</i>	<i>ASTM chamber</i>	<i>50-250^oC</i>	<i>Local retailer</i>
<i>Glue</i>	<i>360</i>	<i>0.5</i>	<i>150 ml Glass vials</i>	<i>50-250^oC</i>	<i>Local retailer</i>
<i>Plywood</i>	<i>160</i>	<i>500</i>	<i>ASTM chamber</i>	<i>50-240^oC</i>	<i>Manufacturer</i>

Figure 2.2 Test Materials in the Headspace bags

Figure 2.3 ASTM Headspace Chamber

Figure 2.4 Photograph of the Test Specimen as received from the supplier

2.4 RESULTS AND DISCUSSIONS

This section deals with the results obtained from the headspace analysis. Sub-section 2.4.1 deals with the results obtained from the adhesive. The headspace results of dry sources are given in sub-section 2.4.2. The chromatogram results obtained from the headspace analysis from each product are shown in figures 2.7 to 2.13. Also a partial list of the identified compounds for each product along with the equilibrium headspace concentration C_{hs} are given in tables 2.9 to 2.15.

2.4.1 Adhesive Headspace Results

Figure 2.5 shows the gas chromatogram of the volatile organic compounds VOCs emitted from the adhesive (*Roberts 900*). A partial list of the identified compounds is given in Table 2.8. As one can see the *GC/MS* analysis indicated that the floor adhesive emits a

rainbow of the VOCs. The emitted compounds have the boiling point ranging from 30 to 220 °C. However, the major compounds identified in the floor adhesive (acetone, nonane, decane, undecane, and dodecane) were used to track the emission in all tests. Except for the first one, all the others belong to the same chemical class namely aliphatic hydrocarbons. Therefore, these major compounds emitted from the adhesive will be targeted in the diffusion measurement phase and in the dynamic chamber testing phase. In the diffusion measurement phase, the diffusion and partition coefficients (D and k_p) of these compounds in the carpet backing material and in the vinyl floor tile were measured. When the emissions from the material assembly (*vinyl // adhesive // substrate*) were analyzed, only these compounds were monitored. In addition to the aforementioned information obtained from the headspace analysis, the last column in Table 2.8 gives the equilibrium headspace concentrations. These equilibrium concentrations were used to estimate the proper air sample volumes for subsequent environmental chamber tests. The air sample in the dynamic chamber tests should contain a VOC mass at least 3 times the detection limit of the analytical system GC/FID. For example, if the detection limit of the GC/FID system is 0.001 µg per sample tube for a VOC of interest, and the concentration of that species in the chamber air is 1.0 µg / m³, then a minimum air sample volume of 0.003 m³ should be collected. It should be pointed out that the headspace results from the adhesive at different sampling times (48, 72, 120, and 192 hours) showed the same chromatograms (*the same peaks*). This implies that, either there are no chemical reactions involved in this type of adhesive during application or curing phase or essentially the same reaction occurs during that period of time. Thus the statement made in section 1.2

of this chapter “*No chemical reaction involved*” was validated in the light of Figures 2.6A-D.

Figure 2.5 Gas Chromatogram of the Adhesive

Table 2.8 Sample of the Identified Compounds in the Floor Adhesive

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Acetone	24.46	23491665	86	134.42
Cyclohexane,1,3,5-trimethyl	33.06	31860339	90	182.30
Cyclohexane,1,2,4-trimethyl	33.53	16415746	94	93.93
Cyclohexane,1,1,2-trimethyl	33.62	16770696	90	95.96
Nonane	33.84	45806174	90	262.10
Cyclohexane,1-ethyl-1-methyl	34.14	35630768	59	203.88
Decane, 2,6,8-trimethyl	34.4	18804305	83	107.60
Nonane, 3-methyl	34.51	28445891	87	162.77
Cyclohexane, propyl	34.6	44825555	83	256.49
Nonane, 4-methyl	35	24693663	70	141.30
Cyclohexane,1,1,2,3-tetramethyl	35.19	26790468	55	153.29
Cyclohexane,1-methyl-3-propyl	35.59	22736247	87	130.10
Decane	35.72	57319118	95	327.98
Decane, 4-methyl	36.1	20861864	91	119.37
Undecane	37.43	14788517	90	84.62
Dodecane	38.55	1800000	91	27.5

Total Volatile Organic Compounds Concentration (TVOC)=6006.54 mg/m³

Figure 2.6A Gas Chromatogram of the emitted species from adhesive after 48 hr

Figure 2.6B Gas Chromatogram of the emitted species from adhesive after 72 hr

Figure 2.6C Gas Chromatogram of the emitted species from adhesive after 120 hr

Figure 2.6D Gas Chromatogram of the emitted species from adhesive after 192 hr

2.4.2 Dry Materials Headspace Results

Partial lists of the major compounds identified from the dry sources tested in this phase are given in Tables 2.10 to 2.16 below. As one can see, the gas chromatograph results presented for these products are very different. For each product the major peaks were chosen for testing in the second and third phases of this thesis research. The equilibrium headspace concentrations C_{bag} and the TVOC (*Total Volatile Organic Compounds*) concentration were also tabulated in the last column of each table. To get a better idea of the contribution of each product to the VOC concentrations indoors, the TVOC concentration produced by each product is compared with that of the floor adhesive. This results in the ratios of r_1 , r_2 , r_3 , r_4 , r_5 , r_6 , r_7 , and r_8 equal 1.0 , 2.4×10^{-4} , 2.8×10^{-2} , 2.3×10^{-2} , 5.9×10^{-2} , 6.5×10^{-5} , 2.3×10^{-4} , 8.1×10^{-5} , respectively, which clearly shows that the dry products TVOC emission concentrations are much smaller than for the floor adhesive (see Figure 2.7). Table 2.9 below summarizes the major identified compounds emitted from the tested products. Also the equilibrium headspace concentrations Y_{bag} (*which were used later to estimate the initial concentration in each product*) and the TVOC of the selected materials are given in the same table.

Before leaving this topic one more point deserves discussion in the light of the headspace results. The carpet and the vinyl flooring headspace results do not contain any of the compounds emitted from the floor adhesive. In other words, neither carpet nor vinyl flooring emits nonane, decane, undecane, or dodecane. This implies that any one of these species detected from the system assembly (*Carpet // Adhesive// Substrate and Vinyl //*

Adhesive // Substrate) is coming from the floor adhesive instead of the carpet or vinyl. A similar argument applies to the plywood headspace result, any benzene, toluene, p-xylene detected in the dynamic chamber testing (*later the plywood will be tested with the recycled tires tile as a composite system, 1/4" Plywood// Recycled Tire Tile// 5/8" Plywood*) is coming from the recycled tires tile instead of the plywood.

Figure 2.7 Comparison of TVOC Headspace concentration of different interior products

Table 2.9 Major Identified Compounds Emitted from the Tested Products

<i>Product Name</i>	<i>Major VOC identified</i>	<i>TVOC (mg/m³)</i>	<i>The Concentration Ratio (r) (relative to the floor adhesive emissions)</i>	<i>The Equilibrium Headspace Concentrations "Y_{bag}" (Avg. of three reading)</i>
<i>Floor Adhesive</i>	1-Nonane 2-Decane 3-Undecane 4-Dodecane	6006.54	1.0	262.10 119.37 84.62 27.50
<i>Gypsum Board</i>	1-Hexanal 2-Heptanal 3-Undecane 4-Nonanal 5-Dodecane 6-Decanal	0.145	0.000024	0.002 0.003 0.003 0.009 0.008 0.013
<i>Particle Board</i>	1-Methyl-Alcohol 2-Pentanal 3-Hexanal 4-Alpha-Pinene 5-Camphene 6-Beta-Pinene 7-Limonene	169.2	0.028	19.6 4.2 13.6 47.1 14.0 4.4 2.7
<i>Sub-floor Tile (Recycled Tiles)</i>	1-Benzene 2-Methyl-iso-Ketone 3-Toluene 4-P-Xylene	142.3	0.023	37.84 10.54 7.54 31.19
<i>Plywood</i>	1-Heptane 2-Octane 3-Alpha-Pinene 4-Camphene 5-Limonene	357.93	0.059	3.51 3.27 73.26 35.82 54.93
<i>OSB</i>	1-Acetic Acid 2-Hexanal 3-Heptanal 4-Furan, 2-pentyl 5-Nonanal 6-Decanal	0.393	0.000065	0.009 0.030 0.006 0.041 0.013 0.010
<i>Carpet</i>	1-Acetone 2-Octanal 3-Nonanal 4-Decanal	13.75	0.0023	1.11 1.01 1.33 0.44
<i>Vinyl Flooring</i>	1-Trichloroethylene 2-Heptanone 3-Octane, 2,2,6-trimethyl 4-4,7-Methano-1H-indene 5-1,4-Cyclooctadiene 6-Naphthalene	0.59	0.000081	0.059 0.016 0.008 0.020 0.003 0.005

2.4.2.1 Gypsum Board Headspace Results

Figure 2.8 Gas Chromatogram of the Gypsum Board Headspace Gases

Table 2.10 Sample of the Identified Compounds in the Gypsum Board

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Hexanal	14.26	538847	47	0.002
Cyclotrisiloxane, hexamethyl-	15.47	772855	53	0.003
Heptanal	18.39	1052036	48	0.003
alpha-Pinene	19.66	1871126	81	0.006
Cyclopropane, pentyl-	21.84	856887	68	0.003
Octanal	22.21	2442436	70	0.008
1-Hexanol, 2-ethyl-	23.19	1226037	50	0.004
Octane, 1-chloro-	24.31	2101744	59	0.007
Undecane	25.66	823582	59	0.003
Nonanal	25.77	2804229	64	0.009
Hexanamide, 6-(heptyloxy)-	27.51	1005379	47	0.003
Dodecane	28.93	2585312	72	0.008
Decanal	29.09	3900461	53	0.013
Decane, 1-chloro-	30.97	597157	53	0.002
Tridecane	31.99	4097526	83	0.013
Dodecane, 1-fluoro-	33.83	725404	64	0.002
Dodecane, 2,6,10-trimethyl-	34.21	822313	59	0.003
Tetradecane	34.86	2167525	90	0.007
Pentadecane	37.40	536388	47	0.002

Total Volatile Organic Compounds Concentration (TVOC)= 0.145 mg/m³

2.4.2.2 Particle Board Headspace Results

Figure 2.9 Gas Chromatogram of the Particleboard Headspace Gases

Table 2.11 Sample of the Identified Compounds in the Particleboard

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Methyl Alcohol	19.31	1067942947	2	19.6
Acetone	19.68	428075260	53	7.9
Pentane	20.21	26009167	64	0.5
Pentanal	22.76	228606682	72	4.2
Hexane, 2,4-dimethyl-	26.78	61406747	74	1.1
Hexanal	27.05	942488373	80	13.6
Tricyclo[2.2.1.0 ^{2,6}]heptane, 1,7,7-trimethyl	34.83	97697781	96	1.8
.alpha.-Pinene	35.98	2560891993	89	47.1
Bicyclo[2.2.1]heptane, 2,2-dimethyl-	36.17	26198802	90	0.5
Camphene	37.03	763172122	97	14.0
.beta.-Pinene	38.97	237020040	94	4.4
3-Carene	41.21	130972945	96	2.4
.alpha.-Terpinene	41.83	59862747	97	1.1
p-Cymene	42.42	119292271	94	2.2
Limonene	42.95	690740360	95	2.7
Bicyclo[3.1.0]hexane,4-methylene-1(1-methylethyl)	43.04	26301415	91	0.5
1,3,6-Octatriene, 3,7-dimethyl-,	43.13	34611001	94	0.6
.gamma.-Terpinene	44.98	52340457	94	1.0
Cyclohexene, 1-methyl-4-(1-methylethylidene)	47.10	146507119	96	2.7
o-Isopropenyltoluene	47.47	108236936	96	2.0
2,4,6-Octatriene, 2,6-dimethyl-	49.73	13205703	93	0.2
1,3-Cyclopentadiene, 1,2,3,4,5-pentamethyl	50.31	14440601	94	0.3

Total Volatile Organic Compounds Concentration (TVOC)= 169.2 mg/m³

2.4.2.3 Sub-floor Tile (Recycled Tires) Headspace Results

Figure 2.10 Gas Chromatogram of the Sub-floor Tile Headspace Gases

Table 2.12 Sample of the Identified Compounds in the Sub-floor Tile

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Acetone	4.39	30051077	56	7.61
Carbon disulfide	4.95	2463733	40	0.65
1-Pentene, 4-methyl-	5.44	4949604	64	1.25
Pentane, 2-methyl-	5.70	9594040	58	2.43
2-Pentene, 2-methyl-	5.80	9775800	90	2.47
2-Butanone	6.59	3190777	64	0.81
Furan, 2-methyl-	6.70	8000667	91	2.03
Benzene	8.63	30006253	94	6.96
Hexane, 2-methyl-	8.92	1871771	58	0.47
Cyclohexene	9.33	14744868	94	3.73
Heptane	10.27	1490986	76	0.38
1-Pentene, 2,4,4-trimethyl-	10.69	3237360	90	0.82
Cyclohexane, methyl-	11.08	2510595	94	0.64
Methyl Isobutyl Ketone	12.22	164103405	90	41.54
Toluene	13.04	25538346	91	6.46
t-Butyl Isothiocyanate	16.57	2684103	53	0.68
Ethylbenzene	17.02	2234404	94	0.57
Methyl Isoamyl Ketone	17.08	3802420	90	0.96
p-Xylene	17.47	117131901	95	31.19
Cyclohexanone	18.39	56005216	95	14.18
Ethanol, 2-butoxy-	19.00	4955199	87	1.25
Benzene, 1-ethyl-2-methyl-	21.00	1569282	90	0.41
Decane	22.47	1380701	92	0.35
Undecane	25.98	1664843	94	0.42
Benzothiazole	30.16	1609519	97	0.41

Total Volatile Organic Compounds Concentration (TVOC)= 142.30 mg/m³

2.4.2.4 Plywood Headspace Results

Figure 2.11 Gas Chromatogram of the Plywood Headspace Gases

Table 2.13 Sample of the Identified Compounds in the Plywood

Compound Name	Retention Time	Area Count	Quality %	(Q)	Concentration (mg/m ³)
Pentane	4.46	2796506	52		20.79
Heptane	10.31	472322	93		3.51
Pentanal	13.04	198113	93		1.47
Octane	14.61	440157	46		3.27
Tricyclo[2.2.1.0 ^{2,6}]heptane,1,7,7-trime	19.51	392793	93		2.92
.alpha.-Pinene	20.02	9853149	91		73.26
Camphene	20.57	4817675	98		35.82
Benzene,1-methyl-2-(1-methylethyl)	21.40	382316	87		2.84
.beta.-Myrcene	22.18	529653	81		3.94
.alpha.-Phellandrene	22.67	1581835	94		11.76
3-Carene	22.90	5481428	96		40.75
.alpha.-Terpinene	23.12	1364536	98		10.15
p-Cymene	23.41	5639517	95		41.93
Limonene	23.58	7387767	87		54.93
.gamma.-Terpinene	24.63	351090	94		2.91
o-Isopropenyltoluene	25.42	248431	96		1.85
Benzene,methyl(1-methylethenyl)	25.67	2180082	95		16.21

Total Volatile Organic Compounds Concentration (TVOC)= 357.93 mg/m³

2.4.2.5 Oriented Strand Board (OSB) Headspace Results

Figure 2.12 Gas Chromatogram of the OSB Headspace Gases

Table 2.14 Sample of the Identified Compounds in the OSB

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Trichloromonofluorometane	4.13	939114	78	0.004
Furan	4.30	694509	59	0.003
Acetic acid	10.53	2305679	86	0.009
Hexanal	14.24	7990516	72	0.030
Cyclotrisiloxane, hexamethyl-	15.43	840243	49	0.003
2-Heptanone	17.93	1446295	40	0.005
Heptanal	18.34	1472953	43	0.006
alpha-Pinene	19.61	845377	64	0.003
2-Heptenal, (Z)-	20.41	1719609	72	0.006
3-Buten-2-ol	21.34	1319868	47	0.005
Furan, 2-pentyl-	21.80	10883178	91	0.041
Octanal	22.17	2007061	50	0.008
Pyrrole	23.18	748652	52	0.003
2-Octenal, (E)-	24.11	1355825	72	0.005
Nonanal	25.71	3584333	64	0.013
Decanal	29.03	2701999	83	0.010
2,4-Nonadienal, (E,E)-	32.41	1144124	46	0.004

Total Volatile Organic Compounds Concentration (TVOC)=0.393 mg/m³

2.4.2.6 Carpet Headspace Results

Figure 2.13 Gas Chromatogram of the Carpet Headspace Gases

Table 2.15 Sample of the Identified Compounds in the Carpet

Compound Name	Retention Time	Area Count	Quality (Q) %	Concentration (mg/m ³)
Sulfur dioxide	20.57	5385383	90	0.24
Methyl formate	22.36	20422353	34	0.90
Acetone	24.48	25232468	80	1.11
Hexanal	31.86	7636211	91	0.34
Cyclotrisiloxane, hexamethyl-	32.03	12318181	90	0.54
1-Nonene	33.68	4604167	91	0.20
Heptanal	33.92	12805447	87	0.56
2-Heptenal	35.00	2832095	81	0.12
Cyclotetrasiloxane, octamethyl-	35.14	7171899	78	0.32
Benzaldehyde	35.23	2894486	97	0.13
Octanal	35.84	23098058	74	1.01
Acetophenone	37.10	7297331	35	0.32
Nonanal	37.61	30246125	83	1.33
Decanal	39.23	10112496	76	0.44

Total Volatile Organic Compounds Concentration (TVOC)=13.75 mg/m³

2.4.2.7 Vinyl Floor Tile Headspace Results

Figure 2.14 Gas Chromatogram of the Vinyl Flooring Tile Headspace Gases

Table 2.16 Sample of the Identified Compounds in the Vinyl Flooring Tile

Compound Name	Retention Time	Quality (%)	Concentration (mg/m ³)
Acetaldehyde	19.63	72	0.033
Methyl Alcohol	19.83	43	0.021
Acetone	20.05	11	0.041
Butanal	20.94	90	0.017
Propanenitrile, 2-methyl-	21.43	83	0.006
Trichloroethylene	22.75	99	0.059
Toluene	24.70	90	0.010
Hexanal	25.85	86	0.004
Cyclotrisiloxane, hexamethyl	26.11	72	0.003
5-3-Heptanone	29.30	95	0.016
Styrene	29.67	93	0.006
Benzene, (1-methylethyl)-	31.13	91	0.004
Hexanal, 2-ethyl-	32.56	64	0.007
Octane, 2,2,6-trimethyl-	32.71	64	0.008
Bicyclo[2.2.1]hept-2-ene, 5-ethenyl-	33.57	90	0.002
4,7-Methano-1H-indene,3a,4,7,7a-tetr	35.83	83	0.020
Limonene	36.41	56	0.006
Indane	36.77	81	0.012
Heptane, 2,2-dimethyl-	37.46	59	0.008
Hexane, 2,2,5-trimethyl-	37.96	64	0.016
1,4-Cyclooctadiene	40.89	64	0.003
Naphthalene	44.63	94	0.005

Total Volatile Organic Compounds Concentration (TVOC)= 0.590 mg/m³

Chapter III

MEASUREMENTS OF THE DIFFUSION AND PARTITION COEFFICIENTS

3.1 INTRODUCTION

This chapter deals with the measurements of the diffusion and partition coefficients (D and k_p) through the test materials. It is divided into three main sections. In the first section (section 3.2) the theory used for the determination of the internal diffusion coefficient (D) and partition coefficient (k_p) of volatile organic compounds (VOCs) through the dry building materials is described. It is divided into three main sub-sections. In sub-section 3.2.1 the theory employed and some theoretical background about the adsorption/desorption theory are discussed. Sub-section 3.2.2 describes the Laplace transformation techniques used for solving the transient diffusion equation. Finally sub-section 3.2.3 describes a step by step procedure used for measuring the diffusion and partition coefficients.

Section 3.3 is devoted to describing the test materials, the diffusion test plan, diffusion measurements test procedure, and the experimental set-up. In this section (Section 3.3) an experimental method for the determination of the internal diffusion coefficient (D) and

partition coefficient (k_p) of volatile organic compounds (VOCs) is developed for dry building materials (*such as carpet, vinyl flooring, plywood, ...etc.*). The method is used to determine D and k_p for six aliphatic hydrocarbon species (*heptane, octane, nonane, decane, undecane, and dodecane*) through the backing material of a carpet specimen, vinyl flooring tile, plywood, gypsum board; five aromatic hydrocarbon species (*benzene, toluene, ethyl-benzene, propyl-benzene, and butyl-benzene*) through a vinyl floor tile, particleboard, plywood, and gypsum board; and five aldehyde species (*pentanal, hexanal, heptanal, octanal, and nonanal*) through specimens of plywood, and particleboard. Finally, section 3.5 is devoted to discussing the results obtained from the diffusion measurements. The main results of this chapter are the diffusion and partition coefficients (D and k_p) which will be used in chapter-V as the model-input parameters.

3.2 THEORY

Before explaining the theory used for measuring the diffusion and partition coefficients, it is worthwhile to introduce a very useful term that usually emerges when two different phases come in contact with each other namely a solid/gas interface. A considerable body of knowledge is available in surface chemistry science and literature regarding the solid/gas interface, however the purpose of the next subsection is to relate the formulation principles used in this study to the basic surface chemistry science.

3.2.1 Gas/Solid Interface

Atoms at the surface of a solid exert an attractive force normal to the surface plane. Consequently, at a *gas/solid interface*, the concentration of gas may exceed that in the gas

phase (Axley 1995 and Tompkins 1978) (*the attraction might have a physical or a chemical nature*). The excess concentration at the surface is termed *adsorption*; the solid is the adsorbent and the gas the adsorbate. According to Slejko (1985), we may distinguish three generic types of adsorption: *Exchange, Physical, and Chemical adsorption*. Table 3.1 below summarizes the above mentioned adsorption types. Therefore, the sorption of a species A to an active site S-* may be represented as (Axley 1995);

Where A•S-* is the species in a state bound to an active site and ΔH_{ad} is the heat of adsorption released. For closed systems under steady environmental conditions the rate at which adsorbate molecules bind to active sites will eventually come to equal the rate at which they are released; the concentration of the adsorbate molecules in the gas-phase “C” and the sorbed-phase “C_s” (*mass-species/mass-sorbent*) will remain constant at their respective equilibrium values. These equilibrium values depend on the nature of the adsorbate, adsorbent, and the thermodynamic state of the system. For isothermal conditions at atmospheric pressure, equilibrium relations between these variables identified as *adsorption isotherms* may be represented functionally as $C_{s0} = f(C^*)$ where f is a function that is unique for each species/solid system, and C_{s0} , and C^* are the near-surface concentration, and the gas-phase concentration respectively. Some isotherm models are tabulated in Table 3.2 (Axley 1995).

Table 3.1 The three generic types of adsorption

(I) Exchange Adsorption

* In this type of adsorption one ionic species which is already attached to the surface exchanges ionic charge with others in the bulk air. Therefore, this kind of ionic exchange produces a sort of electrostatic attraction between the adsorbate and the adsorbent.

(II) Physical Adsorption

- * The adsorbate is bound to the adsorbent by relatively weak intermolecular Van der Waals forces.
- * The heat of adsorption associated with this kind of adsorption is expected to be small relative to that associated with chemical adsorption.
- * Physical adsorption may be expected to be a relatively reversible process.
- * The formation of multiple layers of molecules of adsorbate on the surface of the adsorbent are more likely.

(III) Chemical Adsorption

- * This kind of adsorption results from chemical reactions between the adsorbate and the adsorbent.
- * Very strong binding forces are usually involved, since electrons are shared between the adsorbate and the adsorbent.
- * The heat of adsorption associated with chemical adsorption is greater than with physical adsorption.
- * The chemical adsorption may not be a reversible process.
- * Chemical adsorption may be expected to be associated with the formation of a single layer of molecules of adsorbate on the surface of the adsorbent.

Table 3.2 Isotherm models

<i>Isotherm Model</i>	$C_{s0}=f(C^*)$	<i>Constants</i>
<i>Linear</i>	$C_{s0}=k_e C^*$	k_e is the Equilibrium Partition Coefficient
<i>Langmuir</i>	$C_{s0}=(C, k_l C^*)/(1 + k_l C^*)$	k_l is the Langmuir Coefficient
<i>Freundlich</i>	$C_{s0}=k_f (C^*)^{1/n}$	k_f and n are empirical Freundlich Coefficients
<i>Polanyi DR</i>	$C_{s0}=C_s \text{Exp}(-k_D (\text{Ln}(C_{sat}/C^*))^2)$	k_D Dubinin-Radushkevich Coefficient

Modeling adsorption dynamics depends critically on modeling sorption equilibrium accurately. This may be achieved only through careful selection of a candidate isotherm model and empirical determination of model parameters using carefully measured experimental data. For the sorption of trace concentration air-pollutants on building materials the Langmuir model or its low-concentration asymptote, the Linear model are reasonable first candidates (Axley 1995). Therefore, in this study the linear isotherm model ($C_{s0}=k_e C^*$) is used to describe the near surface concentration where, k_e is the equilibrium partition coefficient. It is also assumed that the equilibrium between the surface concentration and the gas phase concentration is achieved instantaneously (*at least relative to the time scale of any measurement taken*). The instantaneous equilibrium assumption ($C_{s0}=k_e C^*$) has been used previously by many other investigators. For example, Little et al. (1994), (1995) used this assumption when they studied the emission from carpets in the full-scale chamber. Similar assumptions were also adopted by Chang et al. (1997) and Tichenor et al. (1991).

Before leaving this topic it is worthwhile to point out that the sorption process at the surface does not violate the usual mass transfer principles since it is a surface phenomenon. The sorbed compound on the material surface can be seen as analogous to the frozen (*Solid*) state of ordinary water in that it has a lower energy level, *i. e.* lower enthalpy, than liquid water. In other words, the molecule adsorbed at the surface does not have the ability (*energy wise*) to diffuse back into the gaseous phase. However, its enthalpy increases as the solid concentration increases.

Sorption of VOC's at the solid surfaces can be regarded as an interaction between the VOC molecule and the solid surface, in which heat is released, and an enthalpy change occurs (*the energy of the adsorbed molecules reduced*). This change in enthalpy is a barrier to the adsorbed molecules which must be overcome for it to diffuse back into the gaseous phase despite the fact that the concentration gradient between the surface layer and the bulk air does exist.

3.2.2 Solution of the Transient Diffusion Equation

In recent years much work has been done both theoretically and experimentally on the transport of gases through solids. Many points of view and objectives have guided this work (*Table A.2 in Appendix A.3 summarizes the literature review pertinent to the topic*). However, among all of these it is generally accepted that the mechanisms of this transport is first the adsorption of the gas at the solid surface, second the molecular diffusion of the compound through the solid and finally, desorption of the gas at the other solid-gas

interface. The second step controls the rate of transport, which is given by Fick's law of diffusion (Eq. 3.1).

Let l be the thickness of a specimen (e.g., a carpet backing material) separating two chambers (see Figure 3.1). The concentration in one compartment (of volume V_2) at the beginning of the experiment is c_0 ; after time t its value decreases to $c_2(t)$ due to diffusion through the test specimen. Meanwhile, the concentration in the other compartment (of volume V_1) rises from the zero initial value to $c_1(t)$; both volumes are stirred so that the concentration is uniform in each compartment.

Figure 3.1 Schematic representation of the two chambers

Let $C(x,t)$ be the concentration of the diffusing substance at time t in the test specimen at a point whose distance is x from the surface. A is the total area of the sample and D is the diffusion coefficient of the specific compound under study. Assuming that the VOC concentration on the specimen (carpet backing) surface is proportional to the

concentration of the compound in contact with this surface (k_e is the equilibrium partition coefficient), we can describe the process by the following set of equations;

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3.1)$$

Boundary conditions (based on the linear isotherm model as discussed in section 3.2.1)

$$\text{At } x=0 \quad C=k_e c_1 \quad (3.2a)$$

$$\text{At } x=l \quad C=k_e c_2 \quad (3.2b)$$

Initial condition

$$\text{At } t=0, \quad 0 \leq x \leq l \quad C=0 \quad (3.2c)$$

Furthermore, by applying the mass balance around each chamber, the concentration in the low and high chambers can be expressed by Eqs. (3.3), and (3.4) respectively. For instance, by applying the mass balance around the upper chamber (*low concentration chamber*) we get,

$$\dot{m}_m = \dot{m}_{out} + \dot{m}_{accum}$$

where

$\dot{m}_m$ is the rate of mass entering the chamber $\{ \dot{m}_m = DA \left(\frac{\partial C}{\partial x} \right)_{x=0} \}$ in (mg/h)

$\dot{m}_{out}$ is the rate of mass purged from the chamber { $\dot{m}_{out} = 0.0$ }

$\dot{m}_{acc}$ is the rate of change of accumulated mass in the chamber { $\dot{m}_{acc} = V \frac{dc_1}{dt}$ }

substituting of $\dot{m}_{in}$, $\dot{m}_{out}$, and $\dot{m}_{acc}$ in the above mass balance equation yields,

$$c_1 = (DA/V_1) \int_0^t \left(\frac{\partial C}{\partial x} \right)_{x=0} dt \quad (3.3)$$

Similarly, it can be derived for the high concentration chamber that;

$$c_2 = c_0 - (DA/V_2) \int_0^t \left(\frac{\partial C}{\partial x} \right)_{x=l} dt \quad (3.4)$$

The system of Eqs. (3.1 to 3.4) can be solved by means of the Laplace-Carson Transformation. Let S , s_1 , s_2 be the Laplace- Carson Transforms of concentrations C , c_1 , c_2 , so that

$$S(x, p) = \ell(C(x, t)) = p \int_0^{\infty} C(x, t) \text{Exp}(-pt) dt \quad (3.5)$$

$$s_1(p) = \ell(c_1(t)) = p \int_0^{\infty} c_1(t) \text{Exp}(-pt) dt \quad (3.6)$$

$$s_2(p) = \ell(c_2(t)) = p \int_0^{\infty} c_2(t) \text{Exp}(-pt) dt \quad (3.7)$$

By transforming Eq. (3.1) an ordinary differential equation is obtained in the form

$$D \frac{d^2 S}{dx^2} = pS - C(x,0) \quad (3.8)$$

Also equations (3.3) and (3.4) are transformed to take the following forms.

$$s_1(p) = \left(\frac{DA}{V_1 p} \right) \left(\frac{dS}{dx} \right)_{x=0} \quad (3.9)$$

and

$$s_2(p) = c_0 - \left(\frac{DA}{V_2 p} \right) \left(\frac{dS}{dx} \right)_{x=L} \quad (3.10)$$

According to the (3.2c) (*The initial condition*) the solution of the ordinary differential equation (Eq. 3.8) has the form;

$$S = \lambda_1 \sinh \left(x \left(\frac{p}{D} \right)^{0.5} \right) + \lambda_2 \cosh \left(x \left(\frac{p}{D} \right)^{0.5} \right) \quad (3.11)$$

Evaluating the integration constants λ_1 and λ_2 with the help of boundary conditions (Eqs. (3.2a), and (3.2b)), results in;

$$s_1(q) = \frac{\alpha_1 c_0}{(\alpha_1 - \alpha_2 / q^2 - 1)q \sin(q) + (\alpha_1 + \alpha_2) \cos(q)} \quad (3.12)$$

And

$$s_2(q) = \frac{(\alpha_1 \cos(q) - q \sin(q)) c_0}{(\alpha_1 \alpha_2 / q^2 - 1)q \sin(q) + (\alpha_1 + \alpha_2) \cos(q)} \quad (3.13)$$

where;

$$q = l(p/D)^{0.5}, \quad \alpha_1 = \frac{k_e A l}{V_1}, \quad \text{and} \quad \alpha_2 = \frac{k_e A l}{V_2} \quad (3.14)$$

If V_1 and V_2 are equal, the sum $(\alpha_1 + \alpha_2)$ in the numerator of the characteristic equation $\tan(q) = (\alpha_1 + \alpha_2)q / (q^2 - \alpha_1 \alpha_2)$, can be replaced to 2α and the product $\alpha_1 \alpha_2$ can be replaced by α^2 .

The inverse transformation of Eqs. (3.12) and (3.13) according to the generalized Heaviside Theorem (Churchill, 1958) yields the relationship for measurable quantities c_1 and c_2 (*The concentration in the chambers above and below the test specimen respectively*).

$$\frac{(c_2 - c_1)}{c_0} = \sum_{i=1}^{\infty} 4\alpha[q_i^2 + \alpha(2 + \alpha)]^{-1} \text{Exp}\{-q_i^2 D t / l^2\} \quad (3.15)$$

Where q_i are the positive roots of the characteristic equation;

$$\tan(q) = \frac{2\alpha q_i}{(q_i^2 - \alpha^2)} \quad (3.16)$$

The infinite series (3.15) converges rapidly, so that for sufficiently large t only the first term q_1 needs to be considered.

$$\frac{(c_2 - c_1)}{c_0} = \frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} \text{Exp}\left(\frac{-q_1^2 Dt}{l^2}\right) \quad (3.17)$$

Taking “Ln” of both sides of the above equation (Eq. 3.17) yields;

$$\text{Ln} \frac{(c_2 - c_1)}{c_0} = \text{Ln} \left\{ \frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} \right\} - \frac{q_1^2 D}{l^2} t \quad (3.18)$$

Hence, from equation (3.18), the dependence of $\text{Ln} \left\{ \frac{c_2 - c_1}{c_0} \right\}$ on t approaches (with large t) a straight line, with the slope;

$$r = \frac{-q_1^2 D}{l^2} \quad (3.19)$$

that intersects the $\text{Ln} \left\{ \frac{c_2 - c_1}{c_0} \right\}$ axis with a negative intercept;

$$u = \text{Ln} \left\{ \frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} \right\} \quad (3.20)$$

On solving Eqs. (3.16), (3.19) and (3.20), the auxiliary parameters, q_I and the quantities D and α can be computed from experimentally determined values r and u . The partition coefficient k_e can then be determined by Equation (3.14) where $\alpha_1=\alpha_2=\alpha$.

3.2.3 Solution Procedure

The following procedure was used:

- (1) From the straight line part of the plot $\ln[(c_2-c_1)/c_0]$ vs. t , the quantities r and u (*the slope and the negative intercept*) were calculated by the least-squares regression method.
- (2) The root q of the characteristic equation (Eq. 3.16) was first computed by using the Bisection method (Hornbeck, R 1975) for selected values of α as shown in Figure 3.2 (*Note: until now the correct values of α and q were unknown*)
- (3) From Eq. 3.20, q_I values were calculated and plotted against α for a given u (*Fig. 3.2 illustrates curves for a set of u values*).
- (4) The values q_I and α corresponding to the intercept between Eq. (3.20) and Eq. (3.16) for the experimentally determined u are the correct q_I and α values.
- (5) Finally, the diffusion (D) and partition (k_e) coefficients were calculated using Eqs. (3.19) and (3.14), respectively.

Table 3.3 below summarizes the equation numbers from which the diffusion and partition coefficients were computed.

Figure 3.2 q_1 vs. α

Table 3.3 Summary of the equations in the order used

Equation#	Equation	variable
3.16	$\tan(q) = \frac{2\alpha q}{(q^2 - \alpha^2)}$	q (First positive root)
3.20	$u = \ln\left\{\frac{4\alpha}{q^2 + \alpha(2 + \alpha)}\right\}$	u (Intercept)
3.19	$r = \frac{-q^2 D}{l^2}$	D (Diffusion coefficient)
3.14	$\alpha = \frac{k_e Al}{V}$	k_e (Partition coefficient)

3.3 EXPERIMENTAL SET-UP AND TEST PROCEDURE

3.3.1 Measurements Test Plan

The table below summarizes the diffusion test plan and shows the chemico- physical properties of the targeted compounds. As one can see, the targeted compounds are classified into three main chemical classes (*1- Aliphatic Hydrocarbons 2- Aromatic Hydrocarbons 3- Aldehydes*). Both the VOC's and the test materials were carefully chosen to meet the following criteria:

- (i) The selection of the targeted VOC's was based on the results of the GC/MS screening of each product (*results of first part*).
- (ii) The targeted compounds have a wide range of molecular size so that the correlation between diffusion coefficient and molecular weight of each product can be developed.
- (iii) The selected species are polar, semi-polar, and non-polar.
- (iv) They cover a wide range of boiling points, and vapour pressure.
- (v) The selected species are the most abundant compounds emitted from wood-stain, glue, wood finishing product, and engineered wood products (Tichenor et. al 1993, Low, M 1996, and Zhang et. al 1996).
- (vi) The selected materials are the most common products used indoors, with different degrees of porosity and surface roughness.
- (vii) Two of these products (*namely, the carpet, and the vinyl tile*) are usually used indoors in the form of material assemblies (*substrate/glue/carpet, or substrate/glue/vinyl tile*). This overlaid layer (*carpet or vinyl tile*) over the glue

dramatically changes the emission profile from that of adhesive alone by working as a resistance to mass transfer (Low 1996, and Clausen et al. 1993). Therefore, the determinations of these resistances (*Diffusivity*) are the most important steps in modeling the emissions from the material assembly.

Table 3.4 Diffusion test plan and physical properties of target compounds

<i>Material</i>	<i>Chemical Class</i>	<i>Compound Name</i>	<i>Polarity</i>	<i>Molecular Weight</i>	<i>Vapor Pressure* (mm-Hg)</i>	<i>Boiling Point °C</i>
(1) Carpet	<i>Aliphatic-Hydrocarbon</i>	<i>Heptane</i>	<i>Non-Polar</i>	100.21	41.18	98
(2) Vinyl Tile		<i>Octane</i>		114.23	12.56	125
(3) Plywood		<i>Nonane</i>		128.26	3.93	151
(4) Particle board		<i>Decane</i>		142.29	1.25	174
(5) OSB		<i>Undecane</i>		156.3	0.35	196
		<i>Dodecane</i>		170.3	0.12	216
(1) Sub floor (Recycled Automobiles Tires)	<i>Aromatic-Hydrocarbon</i>	<i>Benzene</i>	<i>Semi-Polar</i>	84.07	81.4	80
		<i>Toluene</i>		92.14	25.64	110
(2) Plywood		<i>Ethylbenzene</i>		116.25	8.58	136
(3) Vinyl Floor Tiles		<i>Propyl-benzene</i>		120.2	3.02	159.2
(4) Gypsum board		<i>Butyl-benzene</i>		134.22	0.89	183
(1) Particle-board	<i>Aldehyde</i>	<i>Pentanal</i>	<i>Polar</i>	86.1	30.88	103
(2) Plywood		<i>Hexanal</i>		100.16	10.00	131
		<i>Heptanal</i>		114.19	3.10	153
		<i>Octanal</i>		128.22	1.02	171
		<i>Nonanal</i>		142.24	0.32	195
		<i>Decanal</i>		156.29	0.09	208

* Vapour pressure of all compounds at 23 °C

3.3.2 Experimental Set-up

For the purpose of this study, a new test system facility was designed and constructed at the Institute for Research in Construction (IRC), National Research Council Canada. (*Schematic figures and the detailed design views of the entire test assembly are given in Appendix A.5*). As with the identification and quantification tests, a strong emphasis is placed on cleaning procedures. The effectiveness of the cleaning is checked by taking a “blank” sample from both chambers before starting the test.

The experimental set-up consists of two identical compartments of 50 l in volume. Each chamber has its own sampling and ventilating port. As shown in Fig (3.3), the specimen separates the two chambers, and the VOC (*or VOCs mixture*) under investigation is introduced into the high concentration chamber. Gas samples are collected from the sampling port of each chamber by drawing the gas through a commercially available sorption tube for collecting VOCs. The sorption tube is 4 mm inside diameter and 229 mm long with three layers of sorbents: glass beads, 150 mg of Tenax TM of 25 to 35 mesh, and 150 mg of 25 to 35 mesh. In order to minimize the sink effect, and any possible reaction, all the test components, which could possibly come in contact with the compound are fabricated from electro-polished, stainless steel. To insure good mixing conditions, each chamber is equipped with a small DC fan. The whole test facility is located in a room which is maintained at a constant temperature of $23 \pm 1^{\circ}\text{C}$.

Figure 3.3 Diffusiometric apparatus

3.3.3 Test Procedure

Before conducting the test, many operations must be performed, such as preparing the VOCs standard mixture, cleaning the test apparatus, checking the background level, and preparing the test specimen.

3.3.3.1 Preparation of the Standard Mixture

A 50 l stainless steel chamber (see Figure 3.4) was used for preparing the standard mixture. The step by step procedure used for preparing the VOCs standard mixture is given below;

- (1) The ASTM chamber was cleaned thoroughly with laboratory detergent and distilled water.

- (2) The gas-tight syringe was inserted through the glass vials septum and 0.1 *ml* of the liquid mixture was withdrawn.
- (3) The syringe content were injected into a small glass dish, and immediately the dish was placed inside the ASTM chamber.

The mass of the VOC standard mixtures used in this study are given in table 3.5 below. Since the time required for complete evaporation of the 0.1 *ml* of liquid VOCs in the ASTM chamber varies from mixture to mixture, an average time of 120 *h* was used for all mixtures. This average time (120 *h*) was based on a series of experiments aimed at investigating various combinations of mixture volume versus the time required for complete evaporation.

Figure 3.4 Standard Mixture tank

Table 3.5 Mass of the standard mixtures

Mixture #	Chemical Class	Compound Name	Weight (g)
Mixture# 1	Aliphatic Hydrocarbon	Heptane	0.1094
		Octane	0.1033
		Nonane	0.1464
		Decane	0.3471
		Undecane	0.4083
		Dodecane	1.0012
Mixture# 2	Aromatic Hydrocarbon	Benzene	0.1126
		Toluene	0.1221
		Ethyl-benzene	0.1327
		Propyl-benzene	0.3002
		Butyl-benzene	0.5979
Mixture# 3	Aldehyde	Hexanal	0.1456
		Heptanal	0.0171
		Octanal	0.1515
		Nonanal	0.1525
		Decanal	0.1418

3.3.3.2 Cleaning Procedure

- (1) The two test chambers were cleaned thoroughly with laboratory detergent and distilled water.
- (2) The test chambers were dried using clean lint free cloth.
- (3) The complete test apparatus was cleaned with Methyl-Alcohol (Methanol), giving strict attention to the internal seams within the test chambers.
- (4) The complete test facility was then rinsed thoroughly with distilled water.
- (5) Again the test facility was dried with clean, lint free cloth.

(6) This procedure was repeated for the sample holder and for all glassware (*including sampling syringe and the glass substrate*), gasket materials or mixing fan accessories, which may contaminate the interior of the test chambers during the test.

3.3.3.3 Background Contamination

(1) The test chambers internal-mixing fans were connected and their operation tested.

(2) The two chambers were connected together as if a real test was being conducted, except there were no volatiles present.

(3) The test facility was flushed with ultra zero compressed air. The flushing stage was performed by connecting the sampling port of both chambers with an ultra zero compressed air cylinder (*the ventilation ports were open*). Then after about 4 hr of flushing with flow rate 500 (ml/min), the air cylinder was closed, and all the test facility ports were closed.

(4) After 24 h, air samples were drawn from both chambers through multi-layer sorbent tubes.

(5) The tubes were then removed and analysed by gas chromatography (GC/FID) to determine if there was any residual contamination of the test facility.

(6) If there was evidence of significant residual contamination of the test facility, the cleaning procedure was repeated until the contamination had been reduced to an insignificant level.

3.3.3.4 Starting the Test

- (1) After the background contamination level had been confirmed, a 2l air-tight syringe was used to draw 2l from the ASTM chamber (*the tank that contains the standard mixture*).
- (2) Slowly, the syringe contents were injected into the high concentration chamber. This was done slowly and while the ventilation hole was open in order to avoid any increase in the chamber pressure due to injection.
- (3) Immediately, after the injection process, the ventilation hole, and the sampling port were closed. It should be pointed out that the injection process takes in the range of 2-3 minutes.
- (4) Air samples from the high concentration chamber were drawn through a multi-layer sorbent tube. Triplicate samples were usually taken since these samples were to be used to calculate the initial concentration c_0 . For the same reason mentioned above, all the sampling processes were conducted while the ventilation hole was open.

The choice of a proper sampling volume is important because a large sampling volume would create a pressure difference between the two chambers, and the assumption of pure diffusion would no longer be valid, while on the other hand a high sampling volume is desired for measuring low concentrations. A short series of experiments was therefore conducted to investigate various combinations of initial concentration and sample volume. For this study a sampling volume of 50 ml from the high concentration chamber and 150 ml from the low concentration chamber was found to be suitable. Gas samples

collected by the adsorbent tubes were analyzed by a thermal desorption- *GC/FID* system to determine the VOC concentrations in both chambers.

2.3.3.5 Recording

Test data were recorded in standard format as given in figure 3.5. This format contains spaces for all required information.

Data Sheet For Diffusion Test

Test Code

Compound Name

Temp.

Starting Time

Chemical Class

Material Name

Initial Concentration c_0

Time (hr)	Tube#	Area (Count)		Sample Volume (ml)		Concentration		$\ln(c_2 - c_1)/c_0$
		Chamber#1	Chamber#2	V_1	V_2	Chamber#1 c_1	Chamber #2 c_2	

Figure 3.5 Data Sheet for the Diffusion Test

3.3.4 Test Material and Specimen Preparation

Since the results given in this chapter (*the diffusion and partition coefficients*) were to be used in the diffusion model to predict the emission rates from the dry sources, the materials tested here were the same materials that were tested for their VOCs emissions in the small-scale chamber. After the dynamic emission test had been terminated the test specimens, (*sub-floor tile (recycled automobiles tires), plywood, particle-board, carpet, vinyl tile, gypsum board, and the OSB*) were cut into circular specimens (60 mm in diameter), and placed on a glass substrate in an environmentally controlled room with clean air supply for a minimum of 6 months before testing in the diffusion test apparatus. Air conditions were maintained at 23 ± 1 °C and $50\% \pm 5\%$ RH. This allowed VOCs remaining in the specimens to be minimized and the materials to be in equilibrium with the test condition. Special attention was given to the sealing of the specimen edges. As shown in Figure 3.6 Teflon gaskets are used for sealing the edges.

Figure 3.6 Prepared Test Specimen (Carpet)

Figure 3.7 Photograph of the Assembled Diffusiometric apparatus

3.4 ERROR ANALYSIS

Error analysis is the study and evaluation of uncertainty in measurements. Experience has shown that no measurement, however carefully made, can be completely free of uncertainties. As such errors are not mistakes, you cannot avoid them by being very careful. The best you can hope to do is to ensure that errors are as small as reasonably possible, and to have some reliable estimate of how large they are. The challenge of estimating uncertainties and reducing them to a level that allows a proper conclusion to be drawn is a very important part in any experimental measurement.

The diffusion measurement described in this chapter, similar to other experimental measurements, contain a number of random and systematic errors. The literature is very rich with information describing the various sources of errors and how to correct the data to account for these errors. In this section, a discussion of the errors and their impact on the determination of the diffusion and partition coefficients is presented. The uncertainty analysis is mainly based on the procedures described by Taylor, J (1982) and the work of Moffat, R. (1985).

3.4.1 Analysis of the sources of Uncertainty

(1) Uncertainty due to the Tube Sampling (GC/FID)

The overall accuracy of the GC/FID analysis method and the tube sampling procedure described above is about ± 10 to 15% ($E_{GC/FID} \equiv \pm 10$ to 15%). This amount of uncertainty arises from several sources including: (1) uncertainty due to the sample

volume, (2) uncertainty due to the GC/FID integration method, (3) uncertainty due to the calibration procedure and (4) uncertainty due to the GC column.

(2) Uncertainty in the chamber Volume Estimations (V)

As stated earlier all the test facility components are made of electro-polished stainless steel. The dimensions and geometry can be accurate within $\pm 0.5 \text{ mm}$. However, due to the presence of the Teflon gasket in both chambers the vertical dimensions in the chambers may vary slightly depending on the amount of force used for tightening the chambers together. This change in vertical dimension can be estimated to be $3\text{-}5 \text{ mm}$ (*based on the worst case scenario*). Therefore, the resulting uncertainty in the chambers volume estimations (V) is;

$$E_v \cong \pm 1.3\%$$

(3) Uncertainty in the Specimen Thickness Measurement (l)

A Digimatic Indicator (DIS) was used for measuring the specimen thickness (l). The DIS Digimatic Indicator offers a simple and very precise digital reading. The thickness of the test specimen was measured at different positions (*about 20 readings*) and the average reading was obtained via the Data Collection and Processors Unit integrated with the indicator. Since the resolution of the indicator is 0.01 mm and based on the manufacturer's calibration data, the resulting uncertainty with this kind of device is about

$$E_l \cong 2\%$$

(4) Uncertainty due to the Complete Mixing Assumption

A number of preliminary tests were conducted for the purpose of refining the experimental procedures and determining the most suitable initial concentration and sampling volume. The main points of concern were the homogeneity of the concentration inside the two chambers and the repeatability of the test data. To simplify the analysis of the test results it is convenient to assume that the extracted air sample is representative of the air throughout the test chambers. In other words, it is assumed that the VOC's are homogeneously distributed throughout the air volume of the two chambers. The first objective of the preliminary experiments was therefore to provide for the interior air movement so as to achieve a close approach to homogeneity.

Homogeneity depends on the thoroughness of the air mixing in the chambers. It was argued that lack of homogeneity would reveal itself in the form of poor repeatability from one test to another. An interior air circulation fan was introduced in both chambers to ensure complete air mixing. Such methods have been successfully used in both small and full-scale chambers in which the complete mixing is also critical. Since the circulation fan has been used in each compartment, it can be assumed that the resulting uncertainty is negligible, i. e. $E_{m\alpha} \equiv 0.0$

(5) Uncertainty due to possible Air Leakage

Air leakage is one of the most serious sources of error in the diffusion measurement. Many precautions were made to eliminate air leakage in the test facility. This included: balancing the pressure of both chambers with the ambient pressure (*i. e. the pressure in*

the high concentration chamber, the pressure in the low concentration chamber, and the ambient pressure are equal), taping the specimen/stainless steel interface with more than one layer of Teflon tape (*namely, four Teflon gaskets were used, two above and two underneath the specimen*), and fastening the test specimen to the specimen holder by 12 bolts.

The air tightness of the two chambers was tested by pressurizing the system to constant pressures of 5, 10, 15, 20, 25 and, 30 Pa., and then monitoring (*measuring*) the corresponding air flow rate (Q) required to maintain a specific pressure value. As depicted in Figure 3.8, the flow rate needed to maintain the specific steady pressure is increased with the pressure difference. In other words the leakage rate is increased as the pressure difference is increased. However in this study all the diffusion measurements were conducted at almost zero pressure difference and special attention has been given to the sealing. Therefore, it can be assumed that the resulting uncertainty from the possible leakage is negligible, i. e. $E_{leakage} \cong 0.0$.

Figure 3.8 Air tightness of the test facility

(6) Uncertainty due to Possible Sink Effect in the Chamber Walls

Some consideration was also given to the problem of adsorption of volatiles VOC's on the walls of the test chambers (*the sink effect*), and the effect of this on the measured parameters. It was estimated that this complex process would call for extensive experimentation, far outweighing its importance to the end results, and therefore it was decided to leave this avenue of research to some later date. The uncertainty due to possible sink effect is difficult to estimate since it would be expected to vary with the physical properties of the compound under study. However, based on some previous sink studies for characterizing the sink strength of an empty chamber (An, et al. 1998) it is estimated that the average resulting uncertainty due to possible sink effect is very small and thus, can be neglected for compounds investigated in this study. ($E_s \cong \pm 0.0\%$)

(7) Uncertainty due to Possible Fluctuation of the Ambient Conditions (T, RH)

As already known, the diffusion coefficient is a function of temperature. The temperature and relative humidity measurements are accurate within ± 1 °C, and $\pm 5\%$ respectively. The impact of such insignificant fluctuation of the ambient conditions on the measured quantities is negligible. Therefore, we can assume that the resulting uncertainty is negligible, i. e. $E_{T\ RH} \cong 0.0$

3.4.2 Total Uncertainties of the Measured Quantities

Based on the above analysis of uncertainty sources and assuming that the uncertainties from the different sources are independent of each other, the uncertainty involved with the measured quantities can be estimated by using the method described by Taylor, 1982. Suppose the result, D , is a given function of the independent variables $x_1, x_2, x_3, \dots, x_n$. Thus;

$$D = D(x_1, x_2, x_3, \dots, x_n)$$

Let w_D be the uncertainty in the results (D) and $w_1, w_2, w_3, \dots, w_n$ the uncertainties in the independent variables. If the uncertainties in the independent variables are all given the same odds, then the uncertainty in the results (D) having these odds is expressed by Kline and McClintock (1953) as

$$w_D = \left[\left(\frac{\partial D}{\partial x_1} w_1 \right)^2 + \left(\frac{\partial D}{\partial x_2} w_2 \right)^2 + \dots + \left(\frac{\partial D}{\partial x_n} w_n \right)^2 \right]^{0.5} \quad (3.21)$$

To apply the same principle in our case we have to use equation 3.18 that linked the measured quantities (D , and k_e) with the independent variables c_1 , c_2 , c_0 , q_1 , α , l , and t

$$D = \left(\frac{l^2}{q_1^2 t} \right) \ln \left(\frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} \right) - \left(\frac{l^2}{q_1^2 t} \right) \ln \left(\frac{c_2 - c_1}{c_0} \right) \quad (3.22)$$

Evaluating the $\frac{\partial D}{\partial c_1}$, $\frac{\partial D}{\partial c_2}$, $\frac{\partial D}{\partial c_0}$, $\frac{\partial D}{\partial q_1}$, $\frac{\partial D}{\partial \alpha}$, $\frac{\partial D}{\partial l}$, and $\frac{\partial D}{\partial t}$ terms and substituting into Equation (3.21) yields;

$$w_D = \left[\left[\frac{l^2}{q_1^2 t (c_2 - c_1)} E_{c_1} \right]^2 + \left[\frac{-l^2}{q_1^2 t (c_2 - c_1)} E_{c_2} \right]^2 + \left[\frac{l^2}{q_1^2 t c_0} E_{c_0} \right]^2 + \right. \\ \left. \left[\left(\frac{2l}{q_1^2 t} \right) \left(\ln \frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} - \ln \frac{c_2 - c_1}{c_0} \right) E_l \right]^2 + \left[\left(\frac{-l^2}{q_1^2 t^2} \right) \left(\ln \frac{4\alpha}{q_1^2 + \alpha(2 + \alpha)} - \ln \frac{c_2 - c_1}{c_0} \right) E_t \right]^2 \right. \\ \left. + \left[\left(\frac{2l^2}{t} \right) \left(\frac{\ln(q_1^2 + \alpha(2 + \alpha))}{q_1^3} - \frac{1}{q_1^2 + \alpha(2 + \alpha)} \right) E_{q_1} \right]^2 + \left[\left(\frac{l^2}{q_1^2 t} \right) \left(\frac{1}{\alpha} - \frac{2(1 + \alpha)}{q_1^2 + \alpha(2 + \alpha)} \right) E_\alpha \right]^2 \right]^{0.5}$$

When the numbers are substituted into the above equation (using the experimental data of Toluene through the vinyl-flooring tile as an example), we get

$$w_D = \left[\overbrace{(8.5407897 \times 10^{-9})^2}^{c_1} + \overbrace{(6.9067456 \times 10^{-8})^2}^{c_2} + \overbrace{(6.05288225 \times 10^{-8})^2}^{c_3} + \overbrace{(4.0145021 \times 10^{-9})^2}^l \right. \\ \left. + \overbrace{(2.0072856 \times 10^{-9})^2}^l + \overbrace{(9.4192813 \times 10^{-9})^2}^{q_1} + \overbrace{(1.861549454 \times 10^{-9})^2}^a \right]^{0.5}$$

Then

$$\frac{w_D}{D} = \pm 18.81\%$$

This calculation illustrates that the overall uncertainty in the diffusion coefficient measurements is about $\pm 18\%$. As can be seen improving the measurements in the values of l for example, would not change w_D/D appreciably. A significant reduction in w_D/D could be obtained by improving the measurements in the values of c_1 , and c_2 (*the main source of uncertainty comes from the analytical method (GC/FID analysis)*). This illustrates the utility of the second-power error analysis equation employed here in determining which variables need most attention in improving the accuracy of the measurements. Therefore, the value of $\pm 18\%$ will be used to correct the measured D , and k_c ($+18\%$ and not -18% because in our experience, the tube analysis method generally overestimates rather than underestimates the correct value)

3.5 RESULTS AND DISCUSSIONS

This section deals with the results obtained from the measurements of the diffusion and partition coefficients of volatile organic compounds (VOC's) through dry building materials. The results are presented in four main subsections. The results of the diffusion measurements of the aliphatic hydrocarbon compounds (*heptane, octane, nonane, decane, and undecane*) through the backing material of a carpet specimen, vinyl flooring tile, and the OSB are presented in the first subsection (*section 3.5.1*). The second subsection (*section 3.5.2*) is devoted to the results of the aromatic hydrocarbon compounds namely, *benzene, toluene, ethyl-benzene, propyl-benzene, and butyl-benzene*, through the gypsum board, vinyl flooring tile, sub-floor tile (*recycled tires*), plywood, and particle board. The third subsection, *section 3.5.3* is used to present the results of the diffusion measurements of four aldehyde species (*pentanal, hexanal, heptanal, and octanal*) through particleboard and plywood specimens. Finally, subsection 3.5.4 is used to discuss the results of the diffusion measurements.

3.5.1 D and k_p for the Aliphatic Hydrocarbon Compound Class

The diffusion coefficients were measured for five aliphatic hydrocarbon species (*heptane, octane, nonane, decane, and undecane*) diffusing through the backing material of a carpet specimen, Vinyl flooring tile, and the OSB. The experimental results for selected compounds are shown in Figures 3.9, 3.10 and 3.11 for carpet, vinyl floor tile and the OSB, respectively. The parameter values (D and k_p) for each compound are given in Tables 3.6, 3.7 and 3.8, respectively. As shown in Tables 3.6, 3.7 and 3.8 the range of

measured values of “ D ” for carpet is 5.55×10^{-11} to $2.8 \times 10^{-12} \text{ m}^2/\text{s}$ for the compounds with molecular weights varying between 100 and 157. For the vinyl floor tile, the range of measured values of “ D ” is 2.35×10^{-11} to $2.01 \times 10^{-12} \text{ m}^2/\text{s}$ for the compounds with molecular weight varying between 100 and 157. For the OSB, the range of measured values of “ D ” is from 2.34×10^{-10} to $7.24 \times 10^{-12} \text{ m}^2/\text{s}$, for the compounds with the same range of molecular weight as for the other tests. The largest molecule has the smallest diffusion coefficient, which is true for all three materials tested. And the compounds with highest vapour pressure values at a given temperature (*i. e. most volatile*) have the smallest partition coefficients.

Table 3.6 Parameters for the carpet backing material

Compound Name	Molecular Weight (M_w)	Vapour Pressure (mm-Hg) at 23 ^o C	Diffusion Coefficient “ D ” (m^2/s)	Partition Coefficient “ k_e ”
Heptane	100.2	41.18	5.55×10^{-11}	708.55
Octane	114.2	12.56	4.31×10^{-11}	6171.31
Nonane	128.3	3.93	2.83×10^{-11}	6216.05
Decane	142.3	1.25	5.42×10^{-12}	14617.24
Undecane	156.3	0.35	2.79×10^{-12}	24255.90

Table 3.7 Parameters for the Vinyl Floor Tile

Compound Name	Molecular Weight (M_w)	Vapour Pressure (mm-Hg) at 23 ^o C	Diffusion Coefficient “ D ” (m^2/s)	Partition Coefficient “ k_e ”
Heptane	100.2	41.18	2.35×10^{-11}	408.21
Octane	114.2	12.56	1.5×10^{-11}	1421.95
Nonane	128.3	3.93	7.22×10^{-12}	4821.88
Decane	142.3	1.25	2.74×10^{-12}	16072.05
Undecane	156.3	0.35	2.01×10^{-12}	61250.29

Table 3.8 Parameters for the OSB

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _c "
Heptane	100.2	41.18	2.34×10^{-10}	472.47
Octane	114.2	12.56	1.12×10^{-10}	998.94
Nonane	128.3	3.93	4.51×10^{-11}	2369.11
Decane	142.3	1.25	1.07×10^{-11}	12027.74
Undecane	156.3	0.35	7.24×10^{-12}	25931.86

Figure 3.9 $\ln(c_2 - c_1)/c_0$ vs. Time (Carpet)

Figure 3.10 $\ln(c_2 - c_1)/c_0$ vs. Time(Vinyl Flooring)

Figure 3.11 $\ln(c_2 - c_1)/c_0$ vs. Time(OSB)

Figure 3.12 Diffusion Coefficient vs Mw through OSB

Figure 3.13 Diffusion Coefficient vs Mw through Vinyl Flooring

Figure 3.14 Partition Coefficient vs Vapour pressure for OSB

Figure 3.15 Partition Coefficient vs Vapour pressure for Vinyl Flooring

3.5.2 D and k_e for the Aromatic Hydrocarbon Compound Class

In this chemical class, the diffusion coefficient of five aromatic hydrocarbon species (*benzene, toluene, ethyl-benzene, propyl-benzene, and butyl-benzene*) through the gypsum board specimen, vinyl flooring tile, sub-floor tile (*recycled tires*), plywood, and particle board were measured. The experimental results for selected compounds are shown in Figures 3.16, 3.17, 3.18, 3.19 and 3.20 for, the gypsum board, vinyl flooring tile, sub-floor tile (*recycled tires*), plywood, and particle board, respectively. The parameter values (D and k_e) for each compound are given in Tables 3.9, 3.10, 3.11, 3.12, and 3.13, respectively. As shown in the tables, the range of measured values of " D " for the gypsum board is 1.42×10^{-10} to $7.05 \times 10^{-12} \text{ m}^2/\text{s}$ for the aromatic hydrocarbon compounds with molecular weights varying from 84 to 134. For the vinyl floor tile, the range of measured values of " D " was 1.06×10^{-10} to $4.64 \times 10^{-12} \text{ m}^2/\text{s}$ for the aromatic hydrocarbon compounds with molecular weight varying from 84 to 134. For the sub-floor tile, the range of measured values of " D " was from 2.78×10^{-11} to $3.9 \times 10^{-12} \text{ m}^2/\text{s}$, for the compounds with molecular weight varying from 116 to 156. Also for the plywood and the particle board the range of measured values of " D " is from 2.08×10^{-11} to $7.55 \times 10^{-12} \text{ m}^2/\text{s}$ and from 7.33×10^{-10} to $8.97 \times 10^{-12} \text{ m}^2/\text{s}$ respectively. The same trend was observed regarding the relationship between the molecule size and the measured diffusion coefficient. The largest molecule has the smallest diffusion coefficient, which is true for all the materials tested and the partition coefficient (k_e) also increases as the vapour pressure of the compound decreases, at a fixed temperature.

Table 3.9 Parameters for the gypsum board

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Benzene	84.07	81.4	1.42×10^{-10}	416
Toluene	92.14	25.6	6.38×10^{-11}	941
Ethyl-benzene	116.25	8.58	2.77×10^{-11}	1360
Propyl-benzene	120.2	3.02	1.41×10^{-11}	4562
Butyl-benzene	134.22	0.89	7.05×10^{-12}	14031

Table 3.10 Parameters for the Vinyl Floor Tile

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Benzene	84.07	81.4	1.06×10^{-10}	310
Toluene	92.14	25.6	5.42×10^{-11}	539
Ethyl-benzene	116.25	8.58	2.02×10^{-11}	1522
Propyl-benzene	120.2	3.02	8.03×10^{-12}	4520
Butyl-benzene	134.22	0.89	4.64×10^{-12}	13356

Table 3.11 Parameters for the recycled tires sub-floor

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Benzene	84.07	81.4	2.78×10^{-11}	425
Toluene	92.14	25.6	1.09×10^{-11}	2376
P-Xylene	116.25	8.58	3.89×10^{-12}	4675

Table 3.12 Parameters for the plywood

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Benzene	84.07	81.4	2.08×10^{-11}	184
Toluene	92.14	25.6	1.75×10^{-11}	358
Ethyl-benzene	116.25	8.58	5.53×10^{-11}	2476
Propyl-benzene	120.2	3.02	2.16×10^{-11}	3249
Butyl-benzene	134.22	0.89	7.55×10^{-12}	11918

Table 3.13 Parameters for the particle board

Compound Name	Molecular Weight	Vapour Pressure (mm-Hg) at 23 ⁰ C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k,"
Benzene	84.07	81.4	7.33×10^{-10}	266
Toluene	92.14	25.6	2.68×10^{-10}	968
Ethyl-benzene	116.25	8.58	1.05×10^{-10}	1237
Propyl-benzene	120.2	3.02	3.42×10^{-11}	4388
Butyl-benzene	134.22	0.89	8.97×10^{-12}	18042

Figure 3.16 $\ln(c_2 - c_1/c_0)$ vs. Time(Gypsum board)

Figure 3.17 $\ln(c_2 - c_1)/c_0$ vs. Time(Vinyl Flooring)

Figure 3.18 $\ln(c_2 - c_1)/c_0$ vs. Time(Sub-floor Tile)

Figure 3.19 $\ln(c_2 - c_1)/c_0$ vs. Time (Plywood)

Figure 3.20 $\ln(c_2 - c_1)/c_0$ vs. Time (Particle board)

Figure 3.21 Diffusion Coefficient vs M_w through Gypsum board

Figure 3.22 Diffusion Coefficient vs M_w through Plywood

Figure 3.23 Diffusion Coefficient vs M_w through Particle board

Figure 3.24 Partition Coefficient vs Vapour Pressure for Plywood

Figure 3.25 Partition Coefficient vs Vapour Pressure for Vinyl Floor

3.5.3 D and k_p for the Aldehyde Compound Class

The experimental results of the measurements of the diffusion and partition coefficients of four aldehyde species (*pentanal*, *hexanal*, *heptanal*, and *octanal*) through the specimen of particleboard, and plywood are shown in Figures 3.26, and 3.27 respectively. The parameter values (D and k_p) for each compound are given in Tables 3.14, and 3.15, respectively. Again the trend of the measured values of diffusion and partition coefficients with the molecular weight and the vapour pressure are shown in Figures 3.28 through 3.31.

Table 3.14 Parameters for the Particle board

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ^o C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Pentanal	86.1	30.88	3.66x10 ⁻¹⁰	1980
Hexanal	100.2	10.0	7.42x10 ⁻¹¹	2602
Heptanal	114.2	3.1	2.22x10 ⁻¹¹	7714
Octanal	128.2	1.02	1.26x10 ⁻¹²	11591
Limonene	136.2	1.7	1.83x10 ⁻¹¹	5864

* This compound belongs to the terpines class

Table 3.15 Parameters for the Plywood

Compound Name	Molecular Weight (Mw)	Vapour Pressure (mm-Hg) at 23 ^o C	Diffusion Coefficient "D" (m ² /s)	Partition Coefficient "k _p "
Pentanal	86.1	30.88	9.05x10 ⁻¹¹	680
Hexanal	100.2	10.0	3.58x10 ⁻¹¹	1845
Heptanal	114.2	3.1	2.13x10 ⁻¹¹	3117
Octanal	128.2	1.02	1.138x10 ⁻¹¹	9226
Limonene	136.2	1.7	2.27x10 ⁻¹¹	2839

Figure 3.26 $\ln(c_2 - c_1)/c_0$ vs. Time(Particle board)

Figure 3.27 $\ln(c_2 - c_1/c_0)$ vs. Time (plywood)

Figure 3.28 Diffusion Coefficient vs Mw through Particle board

Figure 3.29 Diffusion Coefficient vs. M_w through plywood

Figure 3.30 Partition Coefficient vs Vapour pressure for plywood

Figure 3.31 Partition Coefficient vs Vapour pressure for Particle board

3.5.4 Discussion of the Diffusion Measurement Results

In this chapter the results of the experimental measurements for the determination of the internal diffusion coefficient (D) and the equilibrium partition coefficient (k_e) of three chemical classes (*aliphatic hydrocarbon, aromatic hydrocarbon, and aldehyde*) of volatile organic compounds (VOCs) through the selected dry building materials were presented. The method is used to determine D and k_e for six aliphatic hydrocarbon species (*heptane, octane, nonane, decane, undecane, and dodecane*) through the backing material of a carpet specimen, vinyl flooring tile, plywood and, gypsum board, and for five aromatic hydrocarbon species (*benzene, toluene, ethyl-benzene, propyl-benzene, and butyl-benzene*) through a vinyl floor tile, particleboard, plywood, and gypsum board. And

finally, it is used to evaluate D and k_p for four aldehyde species (*pentanal*, *hexanal*, *heptanal*, and *octanal*.) diffusing through specimens of plywood, and particleboard.

The linearity shown by the measured $\ln(c_2 - c_1)/c_0$ versus time confirmed the validity of the approximation in Eq. (3.18). Diffusion and partition coefficients for VOCs depend on such chemical and physical properties of the compound as the molecular weight, vapour pressure, polarity, etc. Schwöpe et al. (1989) correlated diffusion coefficients for a wide range of VOCs in six polymers as a function of molecular weight, showing that diffusivity increases with the inverse of the molecular weight. As shown in the present results, the largest molecule has the smallest diffusion coefficient, which is true for all the materials tested. The partition coefficient (k_p) is expected to increase as the vapour pressure of the compound decreases. As shown in Tables 3.6, 3.7 and 3.8 and Figures 3.12, and 3.13, undecane has the lowest vapour pressure, and the largest measured value of " k_p ". Based on the measured data, relationships between D and MW and between k_p and P were shown. It should be noted that the trends are shown only to illustrate the relationship between D and MW and between k_p and P . More data are necessary to obtain more accurate correlations. Park et al. (1989) measured the diffusion and partition coefficients for a range of VOCs in Styrene-Butadiene Rubber (*SBR*) (*which is the main component of the carpet backing material*), and found values of " D " varying between 2.3×10^{-12} and $1.0 \times 10^{-12} \text{ m}^2/\text{s}$, and k_p varying between 200 and 28000 for molecular weights varying from 72 to 166. Little et al. (1994) also studied the emission from carpet in the full-scale chamber, and fit the data to a mass transfer based model. They calculated the diffusion, and partition coefficient for the VOCs with molecular weight varying from

30 to 158, obtaining " D " ranging from 0.5×10^{-12} to $1.0 \times 10^{-11} \text{ m}^2/\text{s}$, and the value of " k_p " varying from 1400 to 170000. These values are close to those obtained from this experimental study. Furthermore, in the study aimed at experimentally measuring the diffusion and equilibrium partition coefficients Little, et al. (1999) measured the values of D and k_p of styrene through the vinyl floor tile. They found that the value of D of styrene through vinyl tile is $1.23 \times 10^{-13} \text{ m}^2/\text{s}$ compared with a value found in this study. It should be pointed out that the variations of D with MW and k_p with P for the carpet backing material do not follow the same trend as for the other products tested in this study. This may be attributed to the effect of the fibers at the carpet surface.

Chapter IV

MEASUREMENT OF VOC EMISSION CHARACTERISTICS USING DYNAMIC ENVIRONMENTAL CHAMBERS

4.1 INTRODUCTION

In this chapter, the experimental methods, the test facility and the results are presented for both dry and wet materials. These experiments were conducted for the purpose of understanding the VOC emission characteristics and for providing reliable data to validate the models developed in this study. In this research, a mass transfer based model is developed for characterising the VOC emissions from dry building materials. A diffusion model is first developed to describe the emissions of volatile organic compounds (VOCs) from the single, individual sources. Then the formulation is extended to include the emissions from composite sources (*system comprising an assemblage of individual sources*). The key parameters for the model (*The diffusion coefficient of the VOC in the*

source material D , and the equilibrium partition coefficient k_e) were determined independently (*model parameters are determined without the use of chamber emission data*). Because the model parameters are measured directly for each component without resorting to dynamic chamber testing, this will substantially reduce the need for standard chamber studies, at least when investigating the diffusion controlled sources. This modelling approach was performed according to the following sequence:

- (1) A headspace study was conducted first to identify the major compounds emitted from the particleboard. Table 2.8 tabulates the most abundant compounds emitted from the particleboard.
- (2) Based on the headspace results, compounds were chosen for diffusion and dynamic measurements in the small-scale chamber.
- (3) A long-term dynamic test (800 hours) was conducted in the small-scale chamber to determine the emission rate as a function of time.
- (4) After being tested for emission rate in the small-scale chamber, a specimen from the particleboard (*from the same specimen tested in the small-scale chamber*) was cut and prepared for the diffusion measurements.
- (5) Based on the headspace results, five compounds (*pentanal, hexanal, heptanal, octanal, and limonene*) were selected for a diffusion measurement study. The diffusion and equilibrium partition coefficients (D , and k_e) of the selected species through the particleboard were measured by using the diffusimetric apparatus described in chapter 3. Table 3.14 summarizes the results of the diffusion measurements through the particleboard.

- (6) With available values for D , k_e , and the initial concentration C_0 in the particleboard, the emission profile was predicted.
- (7) The predicted emission profile was then compared with the experimental chamber observations. Comparing predicted emissions using independently measured parameters to those observed in an experimental chamber will serve as an exceptionally rigorous test of the validity of the current modelling approach.

Three different examples were selected to validate the current modelling approach. In the first example (*Case I*), the model prediction (*using the predetermined model parameters*) was compared with the chamber observation for the particleboard. In the second example (*Case II*) the chamber emission data from the sub-floor (*Recycled Automobile Tires*) was compared with the model prediction. Finally, the third example (*Case III and IV*) was selected to compare the experimental emission data (*from both small and full-scale chamber*) emitted from the composite source (*1/4" plywood // sub-floor tile // 5/8" plywood*) versus the model prediction. In addition, experiments were conducted in a small-scale chamber to generate VOC concentration data for modelling the complex sources namely, the emission from vinyl floor tile and adhesive assembly. The experimental results presented in this chapter will be used to validate the prediction emission models described in chapters V and VI.

4.2 THE TEST FACILITY USED TO GENERATE THE EMISSION DATA

A number of test methods are available to indoor air researchers for characterizing the emissions from the indoor sources (*see table 1.3*). These include, but are not limited to, (1) small chambers (Zhang, et al 1996), (2) large-scale chambers (Zhang et al. 1994), (3) test house, (4) and recently a unique micro-chamber referred to as the Field and Laboratory Emission Cell (*FLEC*) (Wolkoff et al 1991). In this study, experimental data from both small and full-scale chambers were used to validate the current modelling approach. A complete description of the test facilities used for measuring emissions from the sources, including the small-scale chamber, the full-scale chamber, and the Varian Star ex Gas Chromatograph (*GC/FID*) is given in Appendix A.

4.3 EXPERIMENTAL DESIGN

Experiments were designed for the small and full-scale chambers to generate VOC concentration data for the selected product for several hundred hours under controlled experimental conditions. Tests were conducted with the *IRC* test facilities. The facilities allowed accurate control and monitoring of temperature, relative humidity, and airflow rate in the chamber. More details about the test plans, the test condition, and the specimens preparation are discussed in the next sub-sections.

4.3.1 Small Scale Chamber Test Plan

The test plan for the small-scale chamber is given in table 4.1. As shown in the table, some of the designed tests were conducted by using the specimen holder (*namely tests IV,*

V, and VI). The reason for using the specimen holder is to minimize the uncertainty associated with the edges.

Table 4.1 Small Scale Chamber Test Plan

Test Code	Test Duration (hr)	Material	Source Class	Objective
I*	850	Sub-floor tile (<i>Recycled Automobile Tires</i>)	Dry Single Source	i- Model validation ii- The effect of this material on VOC concentration
II	850	Particle-Board	Dry Single Source (Engineered Wood)	i- Model validation ii- The effect of this material on VOC concentration
III*	850	System of 1/4" plywood sheet// Sub-floor tile// 5/8" plywood sheet	Composite Source	i- Model validation ii- The effect of this System on VOC concentration iii- The effect of the plywood layer on the material emission
IV	850	System of 1/4" plywood sheet// Sub-floor Tile (<i>With specimen holder</i>)	Composite Source	i- Model validation ii- The effect of the imperfect contact between the sub-floor tile and the plywood layer
V	850	Glue alone (free surface) (<i>With specimen holder</i>)	Complex Source	i- To determine the diffusion coefficient D of the glue as a function of time. ii- To compare the emission profile with test VI
VI*	850	System of Substrate // Glue // Vinyl (<i>With specimen holder</i>)	Composite complex Source	i- Model validation ii- The effect of this System on VOC concentration iii- The effect of the Vinyl layer on the material emission

* These tests were repeated to check the repeatability of the test procedure

4.3.2 Full Scale Chamber Test Plan

A composite source (*1/4" plywood sheet// sub-floor// 5/8" plywood sheet*) was scaled-up and tested in the full-scale chamber. The test was conducted at 25 °C and 50% relative humidity with 0.5 ACH full exhaust mode. Details of this full-scale chamber are given in Appendix A.2.

4.3.3 Test Condition

An environmental chamber technique, in conjunction with a defined testing protocol, has been designed to accurately assess the VOC's emissions from the test materials. This methodology measures the VOC's emissions using test conditions defined to simulate product use, both residential and commercial, in a realistic manner.

As stated earlier, both small and full-scale chambers were employed. The air supply of the chamber was precisely monitored with regard to quality and quantity. The controlled parameters include chemical purity of the air supply, relative humidity, temperature, and amount of airflow measured in air changes per hour. These parameters are precisely adjusted with a computerized process control system that provides immediate feedback, control, and continuous data logging of the parameters. All of the products were evaluated utilizing consistent, standardized test conditions. The actual measurement conditions, including the chamber system, are given in Table 4.2.

Table 4.2 Environmental Chamber Test Conditions

TEST FACILITY	ENVIRONMENTAL PARAMETERS	SOURCE PARAMETERS
Small Scale Chamber	<ul style="list-style-type: none"> Chamber internal volume 0.41 m^3 Internal mixing within 5% of theoretical perfect mixing condition Standard environmental control that includes <ul style="list-style-type: none"> $1.0\text{ ACH} \pm 0.05\text{ ACH}$ $25.0^\circ\text{C} \pm 0.2^\circ\text{C}$ $50\%\text{ RH} \pm 5\%\text{ RH}$ TVOC background less than $20\text{ }\mu\text{g}/\text{m}^3$ Air velocity over the source surface $8\text{ cm}/\text{sec}$ Low turbulence level 	<ul style="list-style-type: none"> Stainless steel specimen holder was used with test IV, V and VI to minimize the uncertainty associated with the edges Loading factor $0.38\text{ (m}^2/\text{m}^3)$ The following configurations were tested <ul style="list-style-type: none"> Individual dry source Composite source (comprising an assemblage of individual dry sources) Compound sources (comprising an assemblage of glue and vinyl floor tile)
Full Scale Chamber	<ul style="list-style-type: none"> Chamber internal volume 55 m^3 Internal mixing within 2% of theoretical well-mixed model Standard environmental control that include <ul style="list-style-type: none"> $0.5\text{ ACH} \pm 0.05\text{ ACH}$ (Full Exhaust Mode) $25.0^\circ\text{C} \pm 0.2^\circ\text{C}$ $50\%\text{ RH} \pm 5\%\text{ RH}$ TVOC background less than $15\text{ }\mu\text{g}/\text{m}^3$ Air Velocity over the Source Surface $\geq 10\text{ cm}/\text{sec}$ 	<ul style="list-style-type: none"> Only one configuration was tested (14" plywood sheet/ Sub-floor// 5/8" plywood sheet) The chamber loading factor L is equal to 0.08 m^2

4.3.4 Specimen Preparation and Test Procedures

The test specimens were prepared for dynamic testing as follows.

- (1) After being removed from the mylar bag in which they were stored, the materials were cut into the desired dimensions, and returned to their bags for storage in an environmentally controlled room with a clean air supply. Air conditions were maintained at $23 \pm 1^\circ\text{C}$ and $50\% \pm 5\%\text{ RH}$. This allowed VOCs in the specimens to reach the equilibrium condition and the test materials to be in equilibrium with the test condition.

- (2) Immediately before starting the emission test, duplicate headspace samples were taken from the specimen bag. Two types of information are generated from this step. First, the equilibrium headspace concentration C_{bag} will be used to calculate the proper sample volume; this volume must be precisely calculated in order to avoid under or over loading the *GC/FID* column. Secondly, the bag headspace C_{bag} will be used to estimate the initial concentration in the specimen ($C_0 = k_p \cdot C_{bag}$). The initial concentration C_0 is a very important input parameter in the modelling process.
- (3) Then the specimen was placed in the inner chamber, so that the emission surface was flush with the bottom surface of the inner chamber, and the chamber sealed in preparation for gas sampling to begin. The test start time ($t=0$) was established when the door of the chamber was closed.
- (4) VOCs in the chamber outlet were collected on three layer sorbent tubes and analyzed by the *GC/FID*. More than fifty percent of the air samples collected were duplicates. The average relative standard deviation between duplicates was 5% to 17% for individual compounds and 10% for total volatile organic compounds (TVOC's)
- (5) In the case of an adhesive system (*vinyl // glue // substrate*), the mass of the applied adhesive was determined by using a protocol involving weighing of the substrate, the adhesive vial, the paper tissue, the plastic gloves, and the applicator before and after the application. The application method described by Xiangdong Li (1997) was used in

this study to precisely control the amount of glue applied. Then the layer of vinyl was placed over the glue container. Then the whole system was accommodated inside the stainless steel specimen holder. The specimen holder is the stainless steel holder used for holding the test specimen so that only the desired surface area of the specimen is exposed to the air to minimize the uncertainty associated with the edges.

4.4 EVALUATION OF THE SMALL CHAMBER PERFORMANCE

A number of preliminary tests were conducted for the purpose of refining the experimental procedures, determining the most suitable operating parameters, and evaluating the test facility, so that we can have confidence in the observed emission data. The main points of concern were the homogeneity of the airborne concentration inside the test chamber and the repeatability of the test data. Also some consideration was given to the air tightness of the test chamber and the effect of this on the measured data. The next sub-sections will give some details about the evaluation of the small chamber performance.

4.4.1 Air Tightness of the Test Chamber

The air tightness of the test chamber was tested by pressurizing the test facility to a constant gage pressure (30 pa) and then monitoring the change in pressure with chamber leakage rate (*the flow rate required to keep the pressure in the chamber constant*). As can be seen from Figure 4.1 the leakage increases as the pressure inside the chamber increases. This implies that, if a positive pressure of less than 5 Pa is maintained during the test, the air leakage rate will be less than 0.08 l/min , which is equivalent to 0.012 air

exchanges per hour. This leakage rate is well below the air exchange rate used in this study (1 ACH).

Figure 4.1 Air Tightness of the Small Chamber

4.4.2 Mixing Condition

To simplify the analysis of the test results it is convenient to assume that the extracted air sample is representative of the air throughout the test chamber. In other words, it is assumed that the volatiles are homogeneously distributed throughout the air volume of the test chamber. Homogeneity depends on the thoroughness of the air mixing in the chambers. To check the mixing condition, 80 ppb SF_6 (*sulphur hexafluoride*) was injected into the chamber inlet supply air. Then simultaneous air samples from different positions in the chamber were taken (*at the chamber exhaust, chamber bottom, and at the center of the test chamber*). Figures 4.2 and table 4.3 below show the SF_6 concentration

at different locations versus time. The agreement between the SF_6 concentration at different locations implies that the chamber can provide very good air mixing during emission tests and thus the concentration measured at the chamber exhaust is representative of the air throughout the test chamber.

Figure 4.2 SF_6 Concentrations at Different Locations

Table 4.3 Concentrations of SF_6 at Different Positions

Time	Concentration (ppb)					%
min	Exhaust	Bottom	Center	Average (A_v)	S. D	$SD/A_v \times 100$
4	34.921	36.086	33.714	34.907	0.9685	2.7744
6	50.659	54.355	53.638	52.884	1.6003	3.0261
8	61.605	66.140	64.133	63.959	1.8554	2.9010
10	69.218	73.743	69.661	70.874	2.0367	2.8737

4.4.3 Evaluation of the Specimen Holder

The stainless steel holder was used to hold the test specimen so that only the test surface of the specimen is exposed to the air (*this will minimize the uncertainty associated with the edges*). As shown in Figure 4.3, the base part of the holder was equipped with a valve so that the sealing efficiency of the holder can be tested. The performance of the specimen holder was tested by pressurising the holder to 30 Pa gage (*by connecting the inlet valve to the compressed air cylinder*). Then the complete system was immersed into a bath of water. There were no air bobbles detected from the edges (*between the holder and the specimen*), which implies that the edges are completely sealed and only the desired surface area is exposed to the air. Appendix A.4 gives a complete design detail of the specimen holder.

Figure 4.3 Specimen Holder With the Adhesive Container

4.4.4 Background of the Test Chamber

After being thoroughly cleaned (*following the standard method described by ASTM D6330-98*), the test chamber was purged with clean air for a minimum of 24 hours before the test. The background contamination of the chamber was examined after 24 h of flushing at 1 air change per hour using the air purified by the catalytic oxidizer. Air was pumped through the sorption tube at 200 ml/min for 30 minutes. At the end of this period of flushing, the TVOC concentration in the chamber air was found to be below 0.02 mg/m³.

4.4.5 Characteristics of the Flow Field Over the Source Surface

Emission rates for a particular chemical are affected by the concentration of that compound in the boundary layer above the material. This is especially true for materials with high emission rates (*for example, 'wet materials'*), that have the potential to produce concentrations in the boundary layer that are close to the equilibrium concentrations for the particular chemicals. However the boundary layer is determined in part by the air velocity across the material surface. Knowledge of the boundary layer flow characteristics under controlled conditions is essential for establishing realistic airflow conditions for testing and modelling the rates of VOC emissions from the surfaces of building materials and indoor furnishings. There are extensive studies reported in the literature which investigated the velocity indoors. For example, Mathews, et.al. (1989) determined the median air velocity of 5.3 cm/sec in six occupied houses. Gammage and Hawthorne (1985) reported air drift velocities ranging from 1 to 20 cm/sec inside residences. In office settings similar velocities have been reported. 2 to 20 cm/sec with an average of 10 cm/sec reported by Lorch and Straub(1983); 2 to 25 cm/sec with typical values between 10 to 15 cm/sec reported by Hart

and IntHout (1980); and a mean air velocity of 8 *cm/sec* reported by Schiller and Arens(1988). Christianson et.al.(1992) have recommended 10 *cm/sec* for use as a “*standard room condition*” when comparing products used in residences.

In order to maintain a uniform air velocity pattern over the source surface the small environmental chamber is designed so that it will be able to provide adequate control of air velocity and turbulence level as well as the other environmental conditions. As Figure 4.4 shows, the material under investigation is placed in the specimen container so that the specimen surface flushes with the bottom surface of the inner chamber.

Figure 4.4 Position of the test specimen in the inner chamber

This arrangement simulates the flow inside a channel with rectangular cross sectional area. The area affected by viscous effects will grow and meet and encompass the entire flow. Figure 4.5 shows a typical internal flow in a long duct. There is an *entrance region* where a nearly inviscid upstream flow converges and enters the duct. Viscous boundary layers grow

downstream, retarding the axial flow $u(r, x)$ at the wall and thereby accelerating the center-core flow to maintain the continuity requirement. At a finite distance from the entrance the boundary layers merge and the inviscid core disappears. The duct flow is then entirely viscous, and the axial velocity adjusts slightly further until at $x=L_e$ it no longer changes with x and is said to be *fully developed*, $u=u(r)$ only. Downstream of $x=L_e$ the velocity profile is constant, the wall shear is constant, and the pressure drops linearly with x , for either laminar or turbulent flow.

Figure 4.5 Developing velocity profile in the entrance of a duct flow

Dimensional analysis shows that the Reynolds number can be used as the only parameter affecting the entrance length. If

$$L_e = f(d, u, \rho, \mu)$$

Then

$$\frac{L_e}{d} = g(\rho u d / \mu) = g(Re)$$

For laminar flow inside a duct with rectangular cross sectional area the entrance length is given by (Cebeci and Bradshaw 1977) as

$$\frac{L_e}{H} = \frac{Re}{5} \quad (4.1)$$

Where, H is the duct height.

As shown in the previous section a typical velocity measured indoors is 10 cm/sec. If we use $u=10$ cm/sec and $H=8$ cm (*the height of the inner chamber*) then the value of Reynolds number and hence the entrance length can be estimated. Therefore, from Eq.(4.1) with $Re=320$, $L_e=5$ m is obtained. This entrance length ($L_e=5$ m) is relatively high compared with the total length of the inner chamber (55 cm), which implies that the flow is still in the early developing stage, and the two boundary layers are far from the merge point.

In this study the profile of velocity was experimentally measured under well-controlled environmental conditions for the boundary layer flows near the specimen surface. A single component hot wire anemometer probe was used to measure the velocity distribution within the boundary layer. First the hot wire probe was aligned with the flow so that the probe was perpendicular to the airflow direction. This is a very important step for measurement set up since the measurement accuracy is greatly effected by the probe's angle. Then the hot wire was moved perpendicularly to the surface by using a traversing system driven by a stepping motor. The measurements were made at 2.0, 3.0 4.0, 5.0, 6.0,

7.0, 8.0, 9.0, 10.0, 12.0, 15.0, 18.0, 20.0, 23.0, 25.0, 30, 35.0, and 40.0 mm from the surface. In order to reduce the effect of free convection resulting from the temperature difference between the wire and the air, the probe's operating temperature was set at 120 °C instead of 250 °C. The movements of the stepping motor and the data acquisition system were controlled by "ROOMAIR" software. Prior to the test the hot wire anemometer was calibrated for the range of 0.05 to 0.3 (m/sec) by using the TSI 8390 wind tunnel. Complete details for the calibration processes of the hot wire anemometer are given in Appendix B.6. The results were compared with the numerical solutions of the governing equation of motion in the entrance region of the duct with rectangular cross sectional area and with the flow over a flat plate (*Blasius solution*) (Cebeci and Bradshaw (1977) and White, F (1974)). As shown in Figure 4.6 the experimental measurements agree with the numerical solution of the duct flow better than the flow over a flat plate solution.

Figure 4.6 Velocity Profile over the Source Surface

4.5 RESULTS OF THE ENVIRONMENTAL CHAMBERS EMISSION MEASUREMENTS

4.5.1 VOC Emissions from the Particleboard

The results of the experimental chamber observations for the four selected compounds (*hexanal*, *alpha-pinene*, *camphene*, and *limonene*) and TVOC emitted from the particleboard are illustrated in figures 4.7 and 4.8 respectively. The figures indicate that the concentration changes of TVOC and the four major compounds basically followed the same trend. The concentrations first increased to their maximum values in less than 3 hours and then slowly decayed with a different rate for each compound. Almost 50% of the VOC samples collected were duplicates. As illustrated in Table 4.4, the average relative standard deviation between duplicates was 6% to 18% for individual compounds and 10% for TVOC.

Table 4.4 Replicate Sample Analysis for Particleboard

Time (h)	Hexanal ug/m ³	alpha.Pinene ug/m ³	Camphene ug/m ³	Limonene ug/m ³	TVOC ug/m ³
24.10	2.092	1.036	0.274	0.235	5.036
24.10	1.886	1.002	0.218	0.230	4.755
48.26	1.669	0.524	0.097	0.131	4.082
48.24	1.563	0.473	0.083	0.088	3.063
72.18	1.213	0.236	0.045	0.069	2.528
72.18	1.634	0.224	0.051	0.075	2.728
96.03	0.844	0.208	0.042	0.068	3.203
96.03	0.845	0.207	0.040	0.063	3.150
192.10	0.633	0.099	0.022	0.024	2.096
192.09	0.615	0.100	0.013	0.021	2.088
622.39	0.165	0.032	0.005	0.006	0.573
622.81	0.210	0.022	0.006	0.007	0.478
742.40	0.209	0.027	0.004	0.002	0.571
742.83	0.186	0.027	0.003	0.004	0.436

Figure 4.7 Measured Chamber Concentrations for the Four Selected Compounds

Figure 4.8 Measured TVOC Concentration from the Particleboard

4.5.2 VOC Emissions from the Sub-floor Tile (Recycled Automobiles Tires)

The results of the experimental chamber observations for the three most abundant species (*benzene*, *toluene*, and *p-xylene*) and TVOC emitted from the sub-floor tile are illustrated in figures 4.9 and 4.10, respectively. Again the concentration profiles of both TVOC and the individual compounds followed the same trend. As illustrated in Figure 4.10, after 500 hours the TVOC concentration is still well above the chamber background concentration. More than 80% of the VOC samples collected were duplicates. The average relative standard deviation between duplicates was 2% to 7% for individual compounds and 8% for TVOC.

Table 4.5 Replicate Sample Analysis for Sub-floor Tile

Time (hr)	Benzene (mg/m ³)	Toluene (mg/m ³)	P-xylene (mg/m ³)	TVOC (mg/m ³)
24	0.02306	0.04989	0.286	0.414648618
48	0.0171	0.0453	0.2377	0.4580385
48	0.0159	0.0451	0.2293	0.459016393
72	0.0145	0.02525	0.18605	0.289983738
72	0.01455	0.02515	0.1877	0.29565332
96	0.012125	0.014625	0.156525	0.214510174
96	0.0127	0.014725	0.1552	0.212048961
120	0.01145	0.014275	0.1399	0.202286512
120	0.013425	0.014475	0.1454	0.204091219
144	0.011025	0.01385	0.128275	0.177797983
144	0.010825	0.013825	0.128825	0.184217466
168	0.01205	0.014325	0.127225	0.233411528
168	0.012725	0.014	0.12835	0.232296291
216	0.010866667	0.010116667	0.111016667	0.173143835
216	0.011033333	0.01015	0.113316667	0.186653042
240	0.009783333	0.00995	0.106266667	0.171116629
240	0.009816667	0.009883333	0.103133333	0.168585828
264	0.00875	0.009733333	0.099483333	0.147074012
264	0.008383333	0.00965	0.098783333	0.145643798
288	0.0084	0.009633333	0.097533333	0.143296122
288	0.008783333	0.009616667	0.095466667	0.136331839
312	0.008016667	0.009533333	0.0937	0.129655064
312	0.007683333	0.009516667	0.092783333	0.132321379
336	0.007733333	0.009433333	0.090916667	0.133420135
336	0.0089	0.009516667	0.091883333	0.138661202
360	0.00782	0.00923456	0.0836456	0.1434887
360	0.007502483	0.00945254	0.09546	0.1613045
384	0.0077345	0.00914234	0.08073453	0.151605161
408	0.007423546	0.009123	0.0823456	0.153233762
432	0.007153128	0.009251054	0.08345	0.152747867
432	0.00742156	0.00942343	0.0736547	0.153114119
456	0.00704	0.00924356	0.0767556	0.15448146
480	0.0069789	0.009107168	0.072134345	0.153685472

Figure 4.9 Measured VOC Concentrations for the Sub-floor Tile Test

Figure 4.10 Measured TVOC Concentration from the Sub-floor Tile

4.5.3 VOC Emissions from the Material System in the Small Scale Chamber

A photograph of the material system tested in the small chamber is shown in Figure 4.11 below. The sub-floor tile (*the main sources of VOCs*) sandwiched above and underneath low-permeability, zero-concentration $1/4''$ and $5/8''$ plywood layers. The configuration shown simulates the real case scenario of the material system used indoors (*part of floor*). The results of the experimental chamber observations for the three most abundant species (*benzene, toluene, and p-xylene*) emitted from the materials system assembly is illustrated in figures 4.12. The emission profile of the material system assembly will be further discussed in detail in chapter V when the model prediction is compared with the observed chamber data.

Figure 4.11 Photograph of the material system tested in the Small Chamber

Figure 4.12 Measured Chamber Concentrations of VOCs Emitted from the Material System Assembly

4.5.4 VOC Emissions from the Material System in the Full Scale Chamber

The materials system described above (*1/4" plywood // sub-floor tile // 5/8" plywood*) was scaled-up and tested in the full-scale chamber (*loading factor $L=0.08 \text{ m}^{-1}$*). The results of the experimental chamber observations for the three most abundant species (*benzene, toluene, and p-xylene*) emitted from the materials system assembly in the full-scale chamber is illustrated in figures 4.13.

Figure 4.13 Measured Chamber Concentrations of VOCs Emitted from the Material System Assembly in the Full Scale Chamber

It should be pointed out that the imperfect contact between the sub-floor tile and the plywood layers (*the leakage of the pollutants at the interface*) formed the main obstacle for studying and analyzing the emission data from the materials system assemblage. Despite the fact that many precautions were taken to eliminate VOCs leakage at the materials interface, such as using many nails to fasten the materials together, the VOCs leakage at the interface still exists. In order to eliminate the uncertainty associated with the edges namely, the leakage at the interface, another experiment was conducted by using the specimen holder. The main purpose of testing the material system with the specimen holder is to investigate the effect of the assumed VOC leakage at the material

interface on the emission profile. In the current case, the stainless steel holder (*see figure 4.15*) was used to hold the materials assembly (*1/4" plywood // sub-floor tile*) so that only the test surface of the specimen is exposed to the air (*this will eliminate the uncertainty associated with the edges*). Then the materials system was tested in the small-scale chamber. The results of the experimental chamber observations for the three species (*benzene, toluene, and p-xylene*) emitted from the materials system assembly in the small-scale chamber (*with the specimen holder*) are illustrated in figure 4.14.

Figure 4.14 Measured Chamber Concentrations of VOCs from the Material System with Specimen Holder in the Small-Scale Chamber

Figure 4.15 Schematic of the Composite Source in the Specimen Holder

4.5.5 VOC Emission from the Floor Adhesive

This section deals with the result from the adhesive alone (*free surface*) and vinyl tile //adhesive assembly. The result of the emission measurement test from the glue alone in the small- scale chamber is discussed. A hypothesis is offered to explain the double peak profile displayed by the concentration versus time curve from the adhesive alone. Then the results of the experimental chamber observations for the three most abundant species (*nonane, decane and undecane*) emitted from the complex systems assembly (*vinyl // adhesive assembly*) are discussed.

4.5.5.1 The Emission Profile from the Glue Alone

Before presenting the results of the experimental measurements of the glue alone, it is useful to give an overview of the method used to apply the glue on the substrate. In order to control the amount of the glue applied and to reduce the uncertainty associated with the edges, the glue was applied in the stainless steel container following the same procedure described by Xiangdong Li (1997). The application procedure can be summarized in the following steps,

- (1) The weight of the empty container W_1 was determined by using an electronic balance with 1 mg resolution.
- (2) The container was placed in the main base holder as shown in Figure 4.16
- (3) Excessive amount of glue was placed on one side of the main base plate, and the applicator was passed slowly to spread the adhesive uniformly in the container.
- (4) The electronic balance was used again to weigh the container with the adhesive W_2
- (5) The mass of the applied adhesive was determined (10.2 g) by subtracting W_1 from W_2

(6) Immediately, the test specimen was placed in the test chamber. The application procedure took from 2-3 minutes.

Figure 4.16 The glue application method

Initial examination of the emission data from the adhesive alone using the small environmental chamber revealed several interesting features. After almost five hours of the emission, the concentration curves generally display a smoothly decreasing variation, however over the first five hours a strange phenomenon was observed namely the concentrations curve display a double peak profile. As shown in Figure 4.17 the double

peak was observed in all compounds. The following hypothesis is offered with reference to Figure 4.17. Over the first two hours the concentration variation displays the initial transient peak. In this period the skin develops progressively and its porosity decreases, causing a swift reduction in the emission rate. Towards the end of this period the skin porosity has decreased to such an extent that it strongly inhibits the volatile flow, and may actually block this flow completely. The volatiles will continue to evolve or separate from the matrix of the liquid glue. Since these volatiles cannot escape through the skin, or can only escape very slowly, the vapour pressure will build up behind the skin until the pressure is sufficient to open up an escape path, possibly by creating micro-fractures in the skin.

Thus, with reference to Figure 4.17, a sudden rupture of the skin occurs sometime between 2 and 4 hours on the time scale, and there is a fast release of the volatile vapours that have accumulated underneath the skin. Once this fast release is finished, the emission profile settles down to its long-term steady state mode. It should be noted that, in some places on the test specimen the evidence of the skin rupture is very clear even by the naked eye examination.

Figure 4.17 A possible skin blockage and rupture effect

4.5.5.2 Emission from the Complex Systems Assembly

System assemblies such as vinyl flooring // adhesive// substrate are widely used in both commercial and residential environments. The recognition that the presence of the extra resistance on the top of the main source (*the adhesive*) will substantially alter the emission profile has motivated research on the effect of such resistance. Furthermore, the negative impact of such materials on indoor air quality can only be fully understood by examining the total flooring system, which also includes the sub-floor and the adhesive used to fix the flooring to the sub-floor. Adhesives can contain larger quantities of VOCs than the materials they bond. Because of their method of application and use, the emission of VOCs from adhesives and their impact on indoor air quality must be examined in terms of their diffusion through the flooring material and subsequent emission from the flooring

surface. In this study, a set of tests were conducted to examine the effect of the vinyl flooring placed over the adhesive as compared with the adhesive alone, on the rate of emission of the volatile organic compounds which originate with the adhesive. Three tests were conducted. In the first test a specific quantity of the adhesive was spread in a stainless steel container (*following the application procedure described above*) and the emission profile was determined as the adhesive cured for six days. Next a specimen of vinyl flooring tile was placed in the small-scale chamber and the total volatile organic compounds (TVOC) emissions were measured over a six day period. Finally, the emissions profile was measured for a vinyl flooring tile placed on top of a one-hour old layer of adhesive in the stainless steel container as it would be on a floor assembly (*the specimen holder described above was used in order to control the edge effect*).

The emission profiles for the second and third cases are shown in Figure 4.18. The TVOC emission rates from the vinyl flooring alone follow the trend expected from the dry sources. However, examination of the emission rates from the adhesive alone and comparing with the emission rate for the vinyl-adhesive assembly, reveals several interesting features. First, the rate of emissions from the adhesive alone is initially very high, but slows down substantially after about 24 hours. Once covered by the vinyl tile, however a very different response is obtained. Initially, the emissions from the vinyl tile and the vinyl tile + adhesive correspond closely. However, at almost 48 hours, the emissions from the combined system have increased relative to the vinyl-tile alone. This indicates that vinyl tile caused a delay to the escape of the volatiles from the adhesive layer beneath the vinyl tile. So that after 48 hours, the vinyl tile may be saturated with

adhesive VOCs and begins to emit some of these to the air surrounding the tile. Results of these experiments are used to gain insight into the mechanisms controlling the rate of emissions from the system assembly.

Figure 4.18 Chamber emission profile for vinyl tile and vinyl tile- adhesive assembly

The results of the experimental chamber observations for the three most abundant species (*nonane*, *decane* and *undecane*) emitted from the complex systems assembly (*vinyl // adhesive assembly*) are illustrated in figure 4.19. Again the concentration profiles of the selected species followed the same trend.

Figure 4.19 Measured chamber concentrations for the three selected compounds for the complex systems assembly with specimen holder in the small-scale chamber

Chapter V

DEVELOPMENT AND VALIDATION OF A PREDICTION MODEL FOR DRY MATERIAL SOURCES

5.1 INTRODUCTION

The rate of emission of volatile organic compounds from building materials/products may be controlled by a number of variables related to the (1) environmental conditions (*such as air temperature, relative humidity, air velocity, air exchange rate etc.*), (2) nature of the materials (*dry or wet*), and (3) the chemico-physical properties of the pollutants. In order to evaluate the emission characteristics of the material, and improve the indoor air quality, it is desirable to know how these variables influence the emission rate at different stages of the emission process. For modelling purpose, it may be practical to divide the emission process into three main stages: (1) diffusion of a compound through the source material, (2) diffusion of the compound through a boundary layer (*next to the material surface*), and (3) transport and dilution in the bulk air above the source. The physical model which illustrates the aforementioned stages is shown in figure 5.1. Each of

these mass transfer processes (*stages*) can be described by a driving forces divided by a resistance. For instance, in the case of dry sources which include the majority of

Gas-Phase Mass Transfer Rate

Source-Phase Mass Transfer Rate

Figure 5.1 Physical model

materials used to construct and furnish residential and commercial environments, the internal diffusion within the source is the controlling mass transfer mechanism (*Stage 1*). On the other hand if we are dealing with wet sources such as newly applied latex paints, wood stain, caulks and sealant, the emission rate at the early time will be proportional to the difference between the vapour pressure of the compound at the surface and in the surrounding air (*evaporative control mechanism Stage 2*). In this stage the emission rate will be dependent on the level of turbulence, air velocity, and the air exchange rate. Furthermore, the wet sources begin the emissions process under external mass-transfer

control (*Stage 2*), but shortly pass to internal diffusion control as the source dries and hardens. The importance of the diffusion mechanism (*Stage 1*) in the case of wet sources can be briefly seen in the light of experimental observations. In the experiment described by Zhang, et al. (1996) a 0.5 by 0.25 m oak board (*substrate*) was stained and tested in the small environmental chamber which had a volume of 0.4 m^3 . Then based only on the *external mass transfer mechanism* they developed a semi-empirical model to interpret the experimental results. Initial examination of their emission data and model validation revealed several interesting features. First, the concentration of most volatile contaminants in the chamber air quickly reached a peak (*within 2 to 3 hours*) and then decayed rapidly over the next 12 hours. After this period, the decay rates slowed, with emissions of most compounds continuing for the entire time of the experiment (*144 hours*). Using the first 10 hours of the chamber data they found that the evaporative based model fit the data adequately. However, the model prediction failed after 10 hr (*where the diffusion mass transfer mechanism is dominant*). As one can see, this result indicated that the emission rate profile of wet sources consists of two phases, the first decay phase was believed to be mainly controlled by the evaporation process (*in effect for a very short period of time compared with the diffusion-controlled period*). And the second decay phase, which is mainly controlled by the internal diffusion process, is in effect for the rest of the experiment duration. After the first several hours (*externally controlled phase*), the emission process can be considered as being diffusion controlled.

An overview of the significance of diffusional processes has also been stated by many other workers. For instance, Neretnieks et. al. (1993) modeled a hypothetical room in which a PVC flooring material acted as the primary diffusive source of a VOC contaminant. They predicted the rate of release of contaminants by using a linear driving force approximation. In the first case, only the PVC flooring material was considered, while in the second case, the presence of several additional indoor materials was allowed (*including wood, chipboard, cellulose, and polystyrene*). The presence of the other materials substantially prolonged the concentration of the contaminant in the room. They concluded their paper by emphasizing the need to establish a reliable molecular diffusion model for characterizing the emission from dry sources.

In summary, in order to assess the long-term impact of materials/products (*including the wet sources*) on the VOC's concentration and hence the human exposure risk, a diffusion based model is needed. This chapter will discuss the development of a 3-D diffusion based model.

5.2 THEORY AND SOLUTION PROCEDURE

5.2.1 Governing Equations and the Key Assumptions

The governing differential equation describing the three-dimensional transient diffusion through a homogeneous and isotropic source is given by

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (5.1)$$

Where;

$C(x, y, z, t)$ is the concentration of the contaminant in the source (mg/m^3)

t is the time (h)

x, y, z are the linear co-ordinates (m)

D is the diffusion coefficient (m^2/hr)

In the formulation, it is assumed that:

- (1) The volatile contaminant is transported in the source material with a low, constant diffusivity. On the other hand the diffusion coefficients in x, y, z -direction are all equal, and independent of the concentration of the diffusing species.
- (2) There is no chemical reaction involved (*no internal generation*).

Also for the solution, it is assumed that:

- (1) The emitted compound is originally homogeneously distributed within the source material (as described by Eq. 5.2)
- (2) The equilibrium partition coefficient (k_p) between the source surface and the chamber air is also independent of the concentration.
- (3) The volatile contaminant is effectively removed from the upper surface, lower surface, and the edges.

Testing the simplifying assumptions is necessary to a more rigorous validation of the proposed model. The key assumptions stated earlier will be discussed in the light of some previous studies, as well as by some experimental investigations conducted in this research.

The diffusion and partition coefficients are assumed to be independent of VOC concentration in the source. It is known, however, that the coefficients do become concentration dependent as concentrations increase. Schwöpe et al. (1989) have suggested that the concentration dependence on the coefficients may be neglected below a concentration ratio r of 1% ($r = \text{ratio of the initial concentration } C_0 \text{ of VOC to the material density } \rho$). An examination of the observed values of initial concentrations C_0 for all materials tested in this research, show concentration ratio r to be well below this threshold for all cases.

Therefore, based on Schwöpe's results, the assumption that the diffusion coefficient D is independent of concentration C seems justified. A similar argument applies to the use of the partition coefficient, k_p , which also depends on the concentration. At the relatively low contaminant concentrations emitted from the building materials, the use of a constant equilibrium partition coefficient appears reasonable.

Also another key assumption is made in this study regarding the generation term (*or chemical reaction term*). As one can see, the internal generation term was dropped from equation (5.1). This assumption was confirmed via the results of the headspace analysis. The headspace results from the tested products at different times (5, 15, 30, 60 days) show the same chromatograms (*the same peaks*). This implies that, there are no significant chemical reactions involved in this type of materials.

5.2.1.1 Initial Condition

$$C(x, y, z, 0) = C_0(x, y, z) \quad (5.2)$$

5.2.1.2 The Boundary Conditions

For convenience of discussing the development of the boundary conditions, it is worthwhile giving an overview of the numerical method used in solving Eq. (5.1). The numerical technique employed in this study is based on splitting the 3-D problem into three 1-D sub-problems. In other words, in each computation step the problem is treated as a one-dimensional case in the implicit form and only one tridiagonal system is evaluated. For instance, each Δt time interval is further divided into three sub-intervals ($1/3\Delta t$, $2/3\Delta t$, and $3/3\Delta t$). In the first sub-interval ($1/3 \Delta t$) the problem is solved in 1-direction say x -direction with x -direction boundary conditions. And in the second sub-interval ($2/3 \Delta t$) the problem is solved in y -direction with y -direction boundary conditions. Finally, in the third interval ($3/3 \Delta t$) the problem is solved in z -direction of course with z -direction boundary conditions this time. Each time we move from one sub-interval to the next, the previous solutions will be used as the initial values. Therefore, we need 3-sets of boundary conditions, each set corresponding to (or representing) one specific direction. However, only one set of boundary conditions (*one direction*) will be developed here in detail, and the other two sets can be developed in the same manner.

As stated above only the x -direction convective boundary condition will be developed here. In order to account for the boundary layer resistance and to include the environmental variables, mathematical manipulations of the equations are needed. First, a mass balance is applied around the test chamber (See Figure 5.2)

Figure 5.2 Schematic representation of a homogenous source in a chamber

$$\therefore \quad \dot{m}_{emit} = \dot{m}_{acc} + \dot{m}_{out}$$

(5.3)

Where;

$\dot{m}_{emit}$ is the rate of mass emitted from the source

$\dot{m}_{acc}$ is the rate of change of accumulated mass in the test chamber and;

$\dot{m}_{out}$ is the mass rate of VOC's exhausted from the test chamber.

From Eq. (5.3) we get;

$$\dot{m}_{diff} = \dot{m}_{emit} - \dot{m}_{out} \quad (5.3a)$$

Where, $\dot{m}_{diff} = V \frac{dY}{dt}$, $\dot{m}_{emit} = -DA\left(\frac{\partial C}{\partial x}\right)_{x=0}$ and $\dot{m}_{out} = QY$

Eq.(5.3a) can be rewritten as;

$$V \frac{dY}{dt} = -DA\left(\frac{\partial C}{\partial x}\right)_{x=0} - QY \quad (5.3b)$$

or;

$$\frac{dY}{dt} = -DL\left(\frac{\partial C}{\partial x}\right)_{x=0} - NY \quad (5.3c)$$

Where;

Y is the concentration of VOC's in the test chamber

C is the concentration of VOC's in the source

$L=A/V$ is the chamber loading factor (m^{-1})

$N=Q/V$ is the chamber air exchange rate (hr^{-1})

Also at the surface of the source we have;

$$\dot{m}_{diff} = \dot{m}_{conv} \quad (5.4)$$

Where;

$\dot{m}_{diff}$ is the rate of mass diffusion through the solid to the surface.

$\dot{m}_{conv}$ is the rate of mass convected from the source surface

Equation (5.4) can be rewritten as;

$$-D\left(\frac{\partial C}{\partial x}\right)_{x=0} = h\left(\frac{C_{x=0}}{k_c} - Y\right) \quad (5.4a)$$

or

$$Y = \frac{C_{x=0}}{k_c} + \frac{D}{h}\left(\frac{\partial C}{\partial x}\right)_{x=0} \quad (5.4b)$$

Differentiation of Eq. (5.4b) with respect to time gives;

$$\frac{dY}{dt} = \frac{1}{k_c}\left(\frac{\partial C}{\partial t}\right)_{x=0} + \frac{D}{h}\frac{\partial}{\partial t}\left(\frac{\partial C}{\partial x}\right)_{x=0} \quad (5.4c)$$

Substituting Eqs. (5.4b), and (5.4c), into Eq. (5.3c) yields;

$$\frac{1}{k_c}\left(\frac{\partial C}{\partial t}\right)_{x=0} + \frac{D}{h}\frac{\partial}{\partial t}\left(\frac{\partial C}{\partial x}\right)_{x=0} = -DL\left(\frac{\partial C}{\partial x}\right)_{x=0} - N\left\{\frac{C_{x=0}}{k_c} + \frac{D}{h}\left(\frac{\partial C}{\partial x}\right)_{x=0}\right\}$$

or

$$\left(\frac{\partial C}{\partial x}\right)_{x=L} = \left(\frac{-hNC_{x=L}}{k_e D(Lh + N)}\right) - \left(\frac{h}{k_e D(Lh + N)}\right) \left(\frac{\partial C}{\partial t}\right)_{x=L} - \left(\frac{1}{(Lh + N)}\right) \frac{\partial}{\partial t} \left(\frac{\partial C}{\partial x}\right)_{x=L} \quad (5.5)$$

Equation (5.5) is the convective boundary condition in the x-direction where;

k_e is the equilibrium partition coefficient (*dimensionless*)

h is the convective mass transfer coefficient, (*m/hr*)

The second boundary condition at $x=0$ is observed from symmetry to be (*impervious surface*)

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = 0 \quad (5.6)$$

Once again the above boundary conditions (Eqs 5.5 and 5.6) will be used along with Equation (5.7)

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (5.7)$$

in the first sub-interval ($1/3 \Delta t$) to sense the mass diffused in the x-direction. With the x-direction solution array used as an initial condition, equation (5.8) is used along with the y-direction boundary condition (Eqs. 5.8a and 5.8b) in the second sub-interval ($2/3 \Delta t$).

$$\frac{\partial C(y,t)}{\partial t} = D \frac{\partial^2 C(y,t)}{\partial y^2} \quad (5.8)$$

$$\left(\frac{\partial C}{\partial y}\right)_{y=t} = \left(\frac{-hNC_{y=t}}{k_r D(Lh + N)}\right) - \left(\frac{h}{k_r D(Lh + N)}\right) \left(\frac{\partial C}{\partial t}\right)_{y=t} - \left(\frac{1}{(Lh + N)}\right) \frac{\partial}{\partial t} \left(\frac{\partial C}{\partial y}\right)_{y=t} \quad (5.8a)$$

$$\left(\frac{\partial C}{\partial y}\right)_{y=0} = 0 \quad (5.8b)$$

And finally, in the third sub-interval ($3/3 \Delta t$), the z -direction equation (Eq. 5.9) along with the z -direction boundary conditions (Eqs. 5.9a and 5.9b) are used. It should be pointed out that, only after completing the three cycles in each Δt (*after finishing the third sub-interval* $3/3 \Delta t$), is the result available for print out.

$$\frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} \quad (5.9)$$

$$\left(\frac{\partial C}{\partial z}\right)_{z=t} = \left(\frac{-hNC_{z=t}}{k_r D(Lh + N)}\right) - \left(\frac{h}{k_r D(Lh + N)}\right) \left(\frac{\partial C}{\partial t}\right)_{z=t} - \left(\frac{1}{(Lh + N)}\right) \frac{\partial}{\partial t} \left(\frac{\partial C}{\partial z}\right)_{z=t} \quad (5.9a)$$

$$\left(\frac{\partial C}{\partial z}\right)_{z=0} = 0 \quad (5.9b)$$

5.2.2 Computational Domains and Solution Techniques

It will not be possible, within the scope of this study, to present a comprehensive coverage of the various numerical methods for solving partial differential equations. However, the

material presented will provide an introduction to the numerical technique employed here (*splitting the 3-D problem into three 1-D sub-problems*) so that the advantages of the current approach can be justified.

Many different methods of numerical analysis, such as the finite difference, finite element, boundary integral method and Laplace transformations have been presented for solving multi-dimensional transient differential equations. For instance, Bhattacharya (1985) and Lick (1985) applied an improved finite-difference method to solve the transient multi-dimensional heat conduction problem with step by step computation in the time domain. The finite element method based on a variational principle was employed by Gurtin (1964) to analyze the unsteady problem of heat transfer. Bruch and Zyvoloski (1974) solved transient linear and non-linear two dimensional heat conduction problems using the finite-element weighted residual process. Rources and Alarcon (1983) presented a formulation for a two dimensional isotropic continuous solid using the boundary integral equation method with a finite difference approach in the time domain. Chen et al. (1988) successfully applied a hybrid method based on Laplace transformations and a finite difference method to transient heat conduction problems.

The main common factors of the aforementioned methods are the requirements of (i) a complicated procedure, (ii) Large computer storage capacity, and (iii) Long computation times. The first two disadvantages may be accepted. However, the last one (*computation time*) will be the main obstacle in adopting one of the above-mentioned methods. For

instance, the emission from dry sources is likely to have emissions that persist over periods of weeks, months, and even years. And in order to reach the numerical stability by one of the conventional methods, the time step size may have to be reduced to 10^{-4} sec. (*depending on the boundary conditions involved*). As a result, the computational time will accordingly increase. This makes the model impractical for long term prediction. The numerical technique employed in this study not only reduces the computational time, but also maintains a high degree of accuracy.

For convenience of discussion, consider the figure below which illustrates the boundaries and computational domain of a homogeneous source in the (x-y) plane. The first step in the formulation is to subdivide the x, y and z directions into equally spaced nodes, Δx , Δy and Δz respectively. As an approximation we will let the concentration at each node represent the concentration of a cubic element (*compartment*) with volume ($\Delta x \Delta y \Delta z$). A typical set of three consecutive nodes, and the pertinent mass flux terms are illustrated in Figure 5.4.

Figure 5.3 Computational domain of a homogeneous source in (x-y) plane

Figure 5.4 A typical set of three consecutive nodes

In the first sub-time interval ($1/3 \Delta t$) the problem is solved in the x -direction with x -direction boundary conditions (Eqs 5.5, 5.6, and 5.7). In the second sub-time interval ($2/3 \Delta t$) the problem is solved in the y -direction with y -direction boundary conditions (Eqs. 5.8, 5.8a, and 5.8b). Finally, in the third interval ($3/3 \Delta t$) the problem is solved in the z -direction with z -direction boundary conditions (5.9, 5.9a, and 5.9b). As the computation progresses from one direction to the next direction, the previous solutions are used as the initial (*known*) values.

5.2.3 Solution of the Transient Diffusion Equation in the x -Direction

For the reason mentioned earlier, only the solution technique used for solving the transient diffusion in the x -direction will be shown. For the first sub-time interval ($1/3 \Delta t$) equation 5.7, is solved subjected to the initial condition given in equation 5.2 and boundary conditions given by equations 5.5 and 5.6. These equations are solved using a numerical technique based on an integrated finite difference method for solving parabolic partial difference equations. In the present application, the system is represented by a number of cubic compartments in contact with each other. In the current model the air in the space containing the source is represented by one compartment, whereas the source is represented by " j " compartments with thicknesses sequentially divided from bottom to top. This solution gives the concentration of the pollutant in the source as a function of distance, and also of time. The concentration of the contaminant in the chamber air (*the room compartment including the sink effect*) at any time " t " is obtained internally from the same program.

The solution of the transient diffusion equation as discussed in this section is done in two steps. The first step is to obtain a system of ordinary differential equations to formulate the behaviour of the phenomena. Again, this may be done by either a physical formulation or a mathematical formulation. The second step is to obtain a numerical solution to this system of ordinary differential equations (*based on the theory of ordinary differential equations*). The mathematical formulation of the finite-difference method begins with the partial differential equation (Eq. 5.7), plus its boundary and initial conditions (Eqs. 5.2, 5.5, and 5.6). A nodal mesh may be set up just as was shown earlier. Then the second derivative in the differential equation may be replaced by its finite-difference approximation. Both formulations (*physical and mathematical*) will lead to the same system of ODEs. Only the physical formulation of a homogeneous single source will be discussed in detail in the next sub-section.

5.2.3.1 The Physical Formulation

Consider node#1 (*Convective Compartment*) shown below. A mass balance can now be written for the thin cubic compartment in which node#1 is contained. The system shown in Figure 5.3 is elaborated in Figure 5.5 to show the pertinent mass balance terms. The mass balance can be expressed by;

$$\dot{m}_m = \dot{m}_{in} + \dot{m}_{sc} \quad (5.8)$$

Figure 5.5 A typical convective node

$$\dot{m}_{in} = (\Delta y \Delta z) D \left(\frac{C_2 - C_1}{\Delta x} \right) \quad (5.8a)$$

and

$$\dot{m}_{accu} = (\Delta x \Delta y \Delta z) \frac{dC_1}{dt} \quad (5.8b)$$

Finally $\dot{m}_{out}$ is equal to (for the surface node)

$$\dot{m}_{out} = -DA \left(\frac{\partial C}{\partial x} \right)_{x=l} \quad (5.8c)$$

Therefore, from the second boundary condition Eq. (5.5) and Eq. (5.8c) we get

$$\dot{m}_{out} = \Delta y \Delta z \left(\frac{hNC_1}{k_e(Lh + N)} + \frac{h}{k_e(Lh + N)} \frac{\partial C_1}{\partial t} + \frac{D}{(Lh + N)} \frac{\partial}{\partial t} \left(\frac{\partial C_1}{\partial x} \right) \right) \quad (5.8d)$$

It may be observed that the third term of the above equation (5.8d) may be dropped since its order of magnitude is very small compared with the first two terms (*it is multiplied by D, which has a very small value*). Therefore, the mass emitted from the compartment at the surface is given by:

$$\dot{m}_{out} = \Delta y \Delta z \left(\frac{hNC_1}{k_e(Lh + N)} + \frac{h}{k_e(Lh + N)} \frac{\partial C_1}{\partial t} \right) \quad (5.8e)$$

Substitution of equations (5.8a), (5.8b), and (5.8e) into Eq. (5.8) yields;

$$\frac{C_2}{\Delta x / D} - \frac{C_1}{\Delta x / D} - \frac{hNC_1}{k_e(Lh + N)} = \frac{dC_1}{dt} \left(\frac{h}{k_e(Lh + N)} + \Delta x \right)$$

Rearranging terms gives;

$$\frac{dC_1}{dt} = \left(\frac{Dk_e(Lh + N)}{\Delta x(h + \Delta x k_e(Lh + N))} \right) C_2 - \left(\frac{k_e(Lh + N)}{h + \Delta x k_e(Lh + N)} \right) \left(\frac{D}{\Delta x} + \frac{hN}{k_e(Lh + N)} \right) C_1 \quad (5.9)$$

Equation (5.9) is formulated for the boundary of the source namely at the convective side (*Convective Compartment #1*). Similar equations will be used for any other convective nodes such as nodes #6, 11, 16, 21,etc (Figure 5.3).

Next consider the compartments 2,3,4,... (or any other interior nodes). Apply the mass balance in the control volume about cubic compartment “j” where j represents any interior compartment, we get (See Figure 5.4);

$$\frac{C_{j+1} - C_j}{\Delta x / D} = \frac{C_j - C_{j+1}}{\Delta x / D} + \Delta x \frac{dC_j}{dt}$$

Therefore, for compartment #2 for example (j=2),

$$\frac{C_1 - C_2}{\Delta x / D} = \frac{C_2 - C_1}{\Delta x / D} + \Delta x \frac{dC_2}{dt} \quad (5.10)$$

For compartment #3 (j=3)

$$\frac{C_2 - C_3}{\Delta x / D} = \frac{C_3 - C_4}{\Delta x / D} + \Delta x \frac{dC_3}{dt} \quad (5.11)$$

And so on for any other interior nodes.

For compartment #5 (See Figure 5.3) *Impervious boundary*, it must be treated separately, since there is no mass transferred out of the impervious face the mass balance is simply;

$$\dot{m}_{j+1,j} = \dot{m}_{accu}$$

where;

$$\dot{m}_{j+1,j} = D \frac{C_{j+1} - C_j}{\Delta x}$$

and

$$\dot{m}_{accu} = \Delta x \frac{dC_j}{dt}$$

The resulting ordinary differential equation for any impervious compartment is

$$\Delta x \frac{dC}{dt} = \frac{C_{j+1} - C_j}{\Delta x / D}$$

Therefore, for node # 5 for example the ODE will be;

$$\frac{C_4 - C_5}{\Delta x / D} = \Delta x \frac{dC_5}{dt} \quad (5.12)$$

From the above equations, one can observe that, the term $(\Delta x/D)$ is recognized as the mass transfer resistance (R) (*per unit area*) between any two interior compartments (*two nodal points*) and the term (Δx) is recognized as the mass capacitance (T) of the material surrounding the node (*per unit area*). Using this notation, the system of equations then becomes, in dimensional form;

$$\frac{C_2}{R} - C_1 \left[\frac{1}{R} + \frac{Nh}{k_e(Lh + N)} \right] = \left(\frac{h}{k_e(Lh + N)} + \Delta v \right) \frac{dC_1}{dt}$$

$$\frac{C_1 - C_2}{R} - \frac{C_2 - C_3}{R} = T \frac{dC_2}{dt}$$

$$\frac{C_2 - C_3}{R} - \frac{C_3 - C_4}{R} = T \frac{dC_3}{dt}$$

$$\frac{C_3 - C_4}{R} - \frac{C_4 - C_5}{R} = T \frac{dC_4}{dt}$$

$$\frac{C_4 - C_5}{R} = T \frac{dC_5}{dt}$$

Figure 5.6 Mass Transfer Circuit representation

The mass-circuit representation of these equations is shown in Figure 5.6. Initially, each of the concentrations is at the value C_0 (*initial concentration*) at time zero, the switch is

suddenly closed and the system begins to respond. It should be noted here that, close examination of the equation of the first compartment (*convective compartment*) reveals several interesting features. First, the nodal mass transfer resistance in the convective compartment (R_{bound}) consists of two parts, **diffusive resistance** (represented by the term $\Delta x/D$) and **convective or boundary layer resistance** (represented by the term $hN/k_c(Lh+N)$), which are both accounted for in this formulation. Second, the mass transfer capacitance (T_{bound}) also comprises two parts; (Δx) and ($h/k_c(Lh+N)$), which makes this formulation very sensitive to what will happen in the environmental conditions (*such as air velocity, air exchange rate, chamber loading factor,.....etc*). This fundamental formulation (*parameter separation*) will provide a unique opportunity to understand the factors that control the emission process. The impact of each parameter on the emissions from the dry sources can be investigated. For instance, the effect of the air velocity over the source (*boundary layer resistance*) can be investigated by varying the value of h (*the convective mass transfer coefficient*).

The number of ordinary differential equations depends on the number of compartments used (*nodes*). In this research, at least 8000 nodes were used, so a system of ordinary differential equations which comprises 8000 equations, which will give the concentration distribution within the source as a function of time were solved. Since the simultaneous equations are linear, homogenous, and with constant coefficients, the Adam-Moulton method is an ideal technique for solving them [See Appendix C.3 for more details about this method].

5.2.3.2 Layered Composite source

A schematic representation of a layered composite source is given in Figure 5.7. The model for the triple layer system (1/4" Plywood// Recycled Tire tile// 5/8" Plywood) as depicted is a logical extension of the homogeneous slab model described above.

Figure 5.7 Schematic representation of a layered composite source

Equation 5.1, the diffusion equation, applies to each of the three homogeneous layers, or

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right)$$

where i represents layers 1, 2, or 3. Similarly, from the definition of the equilibrium partition coefficient (k_e) we have;

$$k_{e,air} = \frac{(C')_{air}}{Y'}$$

The partition coefficient between the material layers can be represented as;

$$k_{r,p} = \frac{k_{r,air}}{k_{p,air}}$$

Where;

$k_{r,air}$ is the partition coefficient between the recycled tire tile and the air,

$k_{p,air}$ is the partition coefficient between the plywood and the air, and

k_{rp} is the partition coefficient between the recycled tire tile and the plywood.

Also at the interface between the layers the mass fluxes must be equal or for layers 1 and 2 for instance, this may be represented by;

$$D_r \left(\frac{\partial C_r}{\partial x} \right)_{r \text{ side of interface}} = D_p \left(\frac{\partial C_p}{\partial x} \right)_{p \text{ side of interface}}$$

Using the same boundary conditions developed earlier for homogeneous sources, the resulting system of equations (ODE) can be solved (*using the same technique*) to give the

concentration in each layer as a function of time and distance, and hence the gas-phase chamber concentration. Note that the initial condition in each layer is given by:

$$C_r(x, y, z, 0) = C_{r,0}(x, y, z) \quad \text{For Recycled Tire Layer}$$

$$C_{p_1}(x, y, z, 0) = C_{p_1,0} \quad \text{For } 1/4' \text{ Plywood Layer}$$

$$C_{p_2}(x, y, z, 0) = C_{p_2,0} \quad \text{For } 5/8' \text{ Plywood Layer}$$

With available values for D_i , k_{air} and the initial concentration C_{i0} in each layer, the emission profile can be predicted.

Before moving to the next sub-section which discusses the surface sink model used in this study, three important points must be made. The first point regards the importance of the edges when we are modelling the emission from multi-layer sources (*a sandwich style source*). As depicted in Figure 5.7, the presence of the plywood layers on both sides of the main source (*sub-floor tile*) significantly reduces the emission from the main source surface area (*since they act as resistances*). Meanwhile, the main source (*sub-floor tile*) is directly exposed to the environment through the edges. This configuration emphasises the need to give the edges extra attention in order to mimic the real case scenario (*This is why the 3-dimensional formulations were used instead of 1-dimensional*). The second point regards the method used to calculate the mass emitted from each plane (E_z from the *x-y plane*, E_x from the *y-z plane*, and E_y from the *z-x plane*). After the system of equations has been solved, the concentration in each layer as a function of time and distance was determined.

Using the concentration and the rate of change of concentration at the surfaces (Eq. 5.8e) (*surface compartments*), the mass emitted from each plane was determined. For instance, the mass emitted from the plane (x-y) was calculated as following

$$E_{xy} = \sum_{n=1}^n \dot{m}_{out}$$

Where;

n is the number of the compartment forming the (x-y) plane

$\dot{m}_{out}$ is the mass emitted from individual compartment forming the (x-y) plane and it is given by equation (5.8e). Similarly E_x and E_z can be determined from the corresponding equations and the concentrations in surface compartments of the (x-z) and (z-y) planes respectively. Therefore, the total mass emitted from the source at any time ($\dot{m}_{emitted}$) is the algebraic sum of the mass emitted from each individual plane.

$$\dot{m}_{emitted} = E_x + E_y + E_z \quad (5.13)$$

Finally, the third point regarding the equivalent diffusivity D_{eq} is that in order to write the mass balance of any interfacial compartment, in addition to the partition coefficient, the equivalent diffusivity D_{eq} must be used. Consider Figure 5.8, which shows any three consecutive nodes at the interface between the plywood and the sub-floor tile.

Figure 5.8 Nomenclature of the three typical interface compartments

$$\therefore \quad \dot{m}_j = D_p \frac{C_j - C_{\text{int}}}{\Delta z_1 / 2} \quad (5.14)$$

$$\dot{m}_{j+1} = D_r \frac{C_{\text{int}} - C_{j+1}}{\Delta z_2 / 2} \quad (5.15)$$

$$\dot{m}_{int} = D_{eq} \frac{C_{eq} - C_{j+1}}{\Delta z_1 / 2 + \Delta z_2 / 2} \quad (5.16)$$

From Equations 5.14, 5.15, and 5.16 we have;

$$\frac{\dot{m}_j \Delta z_1}{2D_p} = C_{eq} - C_{int} \quad (5.14a)$$

$$\frac{\dot{m}_{j+1} \Delta z_2}{2D_r} = C_{int} - C_{j+1} \quad (5.15a)$$

$$\frac{\dot{m}_{int} (\Delta z_1 + \Delta z_2)}{2D_{eq}} = C_{eq} - C_{j+1} \quad (5.16a)$$

If we add equations (5.14a) and (5.15a) we get

$$\frac{\dot{m}_j \Delta z_1}{2D_p} + \frac{\dot{m}_{j+1} \Delta z_2}{2D_r} = C_{eq} - C_{j+1} \quad (5.17)$$

Observing that, Equation (5.16a) is equal to Equation (5.17) therefore,

$$\frac{\dot{m}_j \Delta z_1}{2D_p} + \frac{\dot{m}_{j+1} \Delta z_2}{2D_r} = \frac{\dot{m}_{int} (\Delta z_1 + \Delta z_2)}{2D_{eq}}$$

Since, $\dot{m}_j = \dot{m}_{j+1} = \dot{m}_{int}$, and $\Delta z_1 = \Delta z_2 = \Delta z$ then;

$$D_{eq} = \frac{2D_p D_r}{D_r + D_p} \quad (5.18)$$

Therefore, for any interfacial compartment j , the mass balance equation is,

$$\dot{m}_{in} = \dot{m}_{out} + \dot{m}_{accum}$$

$$\frac{D_p}{\Delta z^2} C_{i-1} - C_i \left[\frac{D_p}{\Delta z^2} + \frac{D_{eq}}{\Delta z^2} \right] + k_{ip} \frac{D_{eq}}{\Delta z^2} C_{i+1} = \frac{dC_i}{dt}$$

As can be seen the principles of equivalent diffusivity D_{eq} , and the interfacial partition coefficient k_{ip} between the two different materials is included

5.2.3.3 Surface Sink Model

It will be instructive to illustrate the link between the source and the sink surface by using the sample flow chart shown below. Consider a multi-compartment model, as sketched in Figure 5.9. Here we have a three-compartment system, consisting of a room and a sink, driven by a source compartment (*this compartment is further divided into j compartments*). In the context of IAQ modelling, the wallboard, carpet, drapes, or other materials can each be viewed as individual compartments. Materials (*pollutants*) are initially input to the system (*the primary source is the source compartment*), and the compartments exchange these contaminants with one another and the environment, according to dynamics defined by the coupled system of ordinary differential equations (*ODE*).

Figure 5.9 Sketch of three-compartment system

As promised in chapter I, the interaction between the source and the surrounding materials (*the sink effect*) will be included in the formulation. However the sink model adopted in this study is a simple model (*first order reversible sink model*). It is called simple because it is subjected to two severe restrictions: *(i)* the first restriction is that, all the adsorption or desorption process are assumed to occur at the surface of the sink (*i. e. accumulation of the contaminants at the sink surface*). In other words, the accumulated materials (*contaminants*) at the surface do not diffuse into the sink (*no diffusion involved*). This is actually not the case with the building materials used indoors. *(ii)* The second restriction is that the first order reversible sink model can be used only with low concentrations. This restriction (*low concentration*) can be accepted since the emissions from the dry sources are relatively low compared with wet sources. However the

treatment of the sink effect based only on the surface formulation is not consistent with many experimental observations. Conceptually, the adsorption process may be occurring in two stages: first the accumulation of the contaminants at the sink surface then the diffusion of the accumulated contaminants through the pores into the sink materials. It was estimated that this comprehensive formulation (*surface accumulation and internal diffusion*) would call for extensive experimentation, and therefore it was decided to leave this avenue of research to some other worker. In the light of parallel work (*as yet unreported*) by the materials emission team, the wisdom of this decision appears to be confirmed: the process is certainly complex and would require a considerable extension of the routine test procedures. The decision to ignore the diffusion regime in the sink surface, and consider only the surface effects is therefore a weakness of the present study, and a detailed study of these effects (*surface and diffusion*) must be given priority in any follow-up work.

Therefore, the first-order reversible sink model (*the linear form of Langmuir isotherms*) was adopted in this study. Assuming the Langmuir isotherm representation is valid and the occupied adsorption site is only a small fraction of the total available sites, it follows that at equilibrium (Slejko 1985 , and Tichenor et al. 1991)

$$k_a C_e = k_d M_e \quad (5.19)$$

Where,

- k_a is the adsorption rate constant (m/hr)
- k_d is the desorption rate constant ($1/hr$)
- C_e is the equilibrium concentration (mg/m^3)
- M_e is the equilibrium mass adsorbed on the sink (mg/m^2)

Also an equilibrium constant, K_e (m) can be defined as:

$$K_e = k_a/k_d = M_e/C_e \quad (5.20)$$

The mass balance in a perfectly mixed chamber may be written as;

$$\dot{m}_{in} + \dot{m}_{emitted} = \dot{m}_{accum} + \dot{m}_{sink} + \dot{m}_{out} \quad (5.21)$$

Also the mass balance around the sink surface gives

$$\dot{m}_{accumsink} = \dot{m}_{sink} \quad (5.22)$$

Where,

- $\dot{m}_{in}$ is the mass entering to the chamber (*assume perfectly clean air supply, $\dot{m}_{in} = 0$*)
- $\dot{m}_{sink}$ is the mass rate adsorbed by the sink (mg/hr)
- $\dot{m}_{accum}$ is the mass rate accumulated in the chamber air (mg/hr)
- $\dot{m}_{out}$ is the mass rate leaving the chamber through the air exchange flow (mg/hr)
- $\dot{m}_{emitted}$ is the rate of mass emitted by the source (mg/hr)
- $\dot{m}_{accumsink}$ is the rate of mass accumulated at the sink surface

$$\therefore m_{\text{source}} = V \left(\frac{dY}{dt} \right), \quad (5.23)$$

$$\text{and } m_{\text{sink}} = QY, \quad (5.24)$$

$$m_{\text{re-absorb}} = A_s \left(\frac{dM_e}{dt} \right), \quad (5.25)$$

$$m_{\text{sink}} = A_s k_d \left[\frac{M_e}{K_e} - Y \right] \quad (5.26)$$

It should be observed that, m_{emitted} (the mass emitted from the source) may be calculated from Equation 5.13. Therefore, substitution of Equations 5.23, 5.24, 5.26 into Equation 5.21, and Equations 5.25 and 5.26 into Equation 5.22 results in;

$$\frac{dY}{dt} = L m_{\text{emitted}} + L_s k_d M_e - (L_s k_d + N)Y \quad (5.27)$$

$$\frac{dM_e}{dt} = -k_d M_e + k_d Y \quad (5.28)$$

Where,

L is the chamber loading factor ($L = A/V$)

L_s is the sink loading factor ($L_s = A_s/V$)

Thus, if Langmuir adsorption processes are assumed, Equations 5.27 and 5.28 describe the rate of change of concentration and mass in the sink, respectively for the test chamber. As one can observe here, the chamber concentration (*chamber compartment*) including the sink effect is linked with the source compartment through a system of differential equations. The

resulting system of ODE (8002 *differential equations*) was solved simultaneously for the concentrations within the source as well as the test chamber concentration.

5.2.4 Estimation of The Model Input Parameters

The solution of the transient diffusion equation gives the concentration of the pollutant in the chamber air as a function of time and many other parameters. There are ten parameters in this mass transfer based model: C_0 , D , k_e , A , l , h , V , k_a , k_d and, Q . The first five are properties of the source, and the rest are properties of the environment. *(One of the major features of this mass based model is that all the parameters have clear physical definitions and can be either experimentally determined or calculated. The other desirable feature is that each parameter represents a property of either the source or the environment, but not both).* All of the model parameters can be determined or calculated independently. Thus Q , V , and A are all known, while the source thickness " l " was obtained by direct measurement of the source. This leaves the initial concentration " C_0 ", the diffusion coefficient " D ", the convective mass transfer coefficient " h ", and the adsorption and desorption coefficient k_a and k_d to be determined. The next step is to estimate the aforementioned parameters (C_0 , D , k_a , k_d , and h). Usually data from small or large chambers are used to determine the values of model parameters that could give the best agreement between the model prediction and observation (*curve fit techniques*). In this research no fitting will be used and all the model parameters will be independently determined, so that the emissions profile will be predicted a priori and compared with the experimental observations. The next three sub-sections will describe the method used to obtain each parameter (D , C_0 , k_e , h , k_a , and k_d).

5.2.4.1 The Parameters D , C_0 , and k_e

Parameters D , C_0 , and k_e are the most important input model parameters. The theory and the apparatus described in chapter III will be used to obtain D , and k_e . The partition coefficient k_e will be used to determine C_0 , with the assistance of a headspace test. For example, prior to beginning any emission test, the headspace concentration (Y_{bag}) must first be determined. Then by using the equilibrium relationship between the headspace concentration and the equilibrium partition coefficient, the initial concentration C_0 can be estimated as follows:

$$C_0 = k_e \cdot Y_{bag}$$

Where Y_{bag} is the concentration in the bag where the specimen is stored as obtained from the headspace test.

5.2.4.2 The Parameters k_a and k_d

As stated earlier in this research, while this work was going on, another part of the material emissions project team was conducting parallel work aimed at characterizing the sink strength of different materials including the empty stainless steel chamber (*See section 1.2.6.1 in chapter I*). Therefore, the value of k_a and k_d determined from their sink strength test was used in this model.

5.2.4.3 The Parameter h (The Convective Mass Transfer Coefficient)

In most situations, one of the mass transfer resistances (*convective or diffusive resistance*) is much greater than the other, and the smaller of the two resistances can be disregarded. For the dry materials, the internal diffusion resistance within the source (l/D) is the dominant mass transfer resistance and the gas phase resistance (δ/h) can be disregarded. In other words, the velocity over the source surface is immaterial. This conclusion, was confirmed by many workers. For instance N. F. Roache et al. 1994 tested the effect of the air velocity over a *dry* piece of glass substrate waxed with a floor wax by using a FLEC micro-chamber. Two levels of air velocity were used 0.3 *cm/sec*, and 4.5 *cm/sec* (*i. e* two values of *convective mass transfer coefficient* h). Despite an order of magnitude difference in the air velocities, there were no significant differences in the emission rates. These results indicate that the emission processes from the dried wax are controlled by source diffusion and not by gas-phase mass transfer. Furthermore, recently X. Yang and Q. Chen (1998), simulated the emission from a piece of particle-board in the small-scale chamber by using *CFD* (*Computational Fluid Dynamic*). They simulated the emission from one side under three different levels of air velocities 0.005 *m/sec*, 0.03 *m/sec*, and 0.12 *m/sec*, respectively. The emission profiles of all three cases were identical. This implies that the resistance imparted by the boundary layer of the air between the source and the bulk chamber air is very small in the case of dry sources relative to the internal resistance to mass diffusion.

However, for the numerical solution, a number is needed for the convective mass transfer coefficient " h ". Therefore, an average value of 2 *m/hr* was used for all values of h (*The*

convective mass transfer coefficient). The selection of this average value (2 m/hr) is based on the correlation suggested by Spark et al. (1996).

5.2.5 Numerical Solution of the Diffusion Equations

Appendix C.4 Describes the computer program used to solve the internal diffusion problem using the Adams-Moulton method. The rest of this chapter is devoted to the results and validations of the current modelling approach. The results are presented in three main sections. The accuracy of the current numerical approach was demonstrated by comparing the numerical results with the exact solutions of three different examples. Each example was carefully chosen to check a specific aspect of the numerical solution. Section 5.4 is devoted to the general behavior of the model. In this section the general behavior of the model is briefly examined. And the influence of the key model parameters such as C_0 , D , k_c , and h on the resulting contaminant concentration in the air is investigated. Finally, section 5.5 is used to present the results of the experimental validations of the current modeling approach. Three different examples were selected to validate the current modelling approach. In the first example (*Case I*), the model prediction (*using the predetermined model parameters*) was compared with the chamber observation for the particleboard. The second example (*Case II*) the chamber emission data from the sub-floor (*Recycled Automobile Tires*) was compared with the model prediction. Finally, the third example (*Case III and IV*) was selected to compare the experimental emission data (*from both small and full-scale chambers*) emitted from the

composite source (*1/4" plywood // sub-floor // 5/8" plywood*) versus the model prediction.

5.3 VALIDATION OF THE SOLUTION PROCEDURE

As in good numerical analysis practice, whatever numerical method is chosen it should be fully documented as to its step size, stability, and accuracy characteristics, so that confidence in the calculated results for the problem at hand is established. This is especially true since, so-called "*stiff*" systems are not unusual in IAQ modeling. Therefore, to demonstrate the accuracy of the present numerical method, three different examples were selected. Each example was carefully chosen to check a specific aspect of the numerical solution. Since the case of interest here involves a big number of ODEs (*resulting from the physical formulation in chapter 2*), the first example was chosen to demonstrate the ability (*and accuracy*) of the present method for handling a set of stiff ordinary differential equations. A set of two stiff differential equations with well-known exact solution was chosen for the comparison between the numerical solution and the exact one.

The second and the third examples, were selected to check the accuracy of the splitting method (*splitting the 3-D problem into three 1-D problems*) employed here, by comparing the numerical results with exact solutions of simple cases of 2-D and 3-D problems. The similarities between the governing equations for conductive heat transfer and diffusive mass transfer (Eq. 5.1) are noted, suggesting that the exact solution for

conductive heat transfer can be used for diffusive mass transfer, provided the boundary conditions correspond.

5.3.1 Example 1 (Stiff Differential Equations)

Significant difficulties can occur when standard numerical techniques are applied to approximate the solution of a differential equation when the exact solution contains terms of the form $e^{\lambda t}$, where λ is a complex number with a negative real part. This term decays to zero with increasing t , but its approximation generally will not have this property. Unless extreme care is taken, the error associated with the decaying transient portion can dominate the calculations and produce meaningless results. However, in the current numerical approach (*The fifth order Adam-Moulton method*), an error analysis is conducted at each step, and the error estimates are added to the solution for improved accuracy (*this makes it sixth order accurate*). Furthermore, the error array is returned to the main program at the end of each step. One or more of the error array elements was monitored to determine whether a step- size change is required.

The following example will demonstrate the advantages of the fifth order Adam-Moulton method over other methods for handling the stiff system of ODEs. Let us consider the following differential equation

$$\frac{d^2x}{dt^2} + 10001 \frac{dx}{dt} + 10000x = 0 \quad (5.29)$$

With the initial conditions

$$x(0)=1 \quad \frac{dx}{dt} = -1$$

The second order differential equation above can be expressed as the two first order differential equations as

$$\frac{dx}{dt} = -10001x - 10000x \quad (5.29a)$$

$$\frac{dx}{dt} = -x \quad (5.29b)$$

The analytical solution of Eq. (5.29) is

$$x = a e^{-t} + b e^{-10000t} \quad (5.30)$$

The eigenvalues of the system are -1 and -10000. Using the initial condition the constants a and b are found to be

$$a=1 \quad b=0$$

The exact solution is thus

$$x = e^{-t} \quad (5.31)$$

This is a very innocent appearing decaying exponential, and we might expect a numerical solution by almost any of the common methods to give good results. However, using a

step size ($\Delta t = 0.001$) and the double-precision fifth-order Runge-Kutta method, the value of x (the solution) has reached 0.39475×10^{-293} by the time t has reached just 0.2, and computer overflow soon followed.

Reducing the Δt value to 0.0005 yielded no better result. Instability still showed up with the step size reduced to 0.0001. However, the same equation was solved by the fifth-order Adam-Moulton method (Hornbeck 1975) with the error estimates added to the solution, the value of Δt required to reach the stability was only 0.005. The portion of the solution obtained by the fifth-order Adam-Moulton method and the analytical results with $\Delta t = 0.005$ is shown below.

<i>TIME</i>	<i>X-NUMERICAL</i>	<i>X-EXACT</i>	<i>ERR EST X</i>
0	1.000000000000	1.000000000000	
.2	.818749092852	.818749092852	.0000000E+00
.4	.670350077046	.670350077046	.0000000E+00
.6	.548848517475	.548848517475	.0000000E+00
.8	.449369225796	.449369225796	.0000000E+00
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
4.0	.018314563792	.018314563792	.0000000E+00
4.2	.014995032491	.014995032491	.0000000E+00
4.4	.012277169249	.012277169249	.0000000E+00
4.6	.010051921186	.010051921186	.0000000E+00
4.8	.008230001352	.008230001352	.0000000E+00
5.0	.006738306141	.006738306141	.0000000E+00
5.2	.005516982040	.005516982040	.0000000E+00
5.4	.004517024041	.004517024041	.0000000E+00
5.6	.003697684744	.003697684744	.0000000E+00
5.8	.003027476030	.003027476030	.0000000E+00
.	.	.	.
.	.	.	.

.	.	.	.
.	.	.	.
.	.	.	.
8.2	000274673868	000274673868	00000000E+00
8.4	000224888980	000224888980	00000000E+00
8.6	000184096552	000184096552	00000000E+00
8.8	000150728885	000150728885	00000000E+00
9.0	000123409138	000123409138	00000000E+00
9.2	000101041120	000101041120	00000000E+00
9.4	000082727325	000082727325	00000000E+00
9.6	000067732922	000067732922	00000000E+00
9.8	000055456269	000055456269	00000000E+00
10.0	000045397101	000045397101	00000000E+00

5.3.2 Example 2 (Two Dimensional Problem)

In this example the heat dissipation of a square plate is analyzed. Its initial temperature is 30 °C. A boundary surface of the plate is insulated, but the temperature on all other boundaries are kept constant. For simplicity, it is assumed that, $\alpha_x = \alpha_y = 1.25 \text{ m}^2/\text{sec}$, where α is the thermal diffusivity of the plate and $L_x = L_y = 3.0 \text{ m}$, $\Delta x = \Delta y = 0.3 \text{ m}$. Where, L_x and L_y are the lengths of the solution domain in the x and y directions, respectively. Thus, the governing equation, boundary conditions, and the initial condition for this example are given by,

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} \quad \{0 \leq L_x \leq 3.0, \quad 0 \leq L_y \leq 3.0, \quad t \geq 0\} \quad (5.32)$$

$$\theta(0, y, t) = \theta(L_x, y, t) = \theta(x, L_y, t) = 0 \quad (5.33a)$$

$$\left(\frac{\partial \theta}{\partial y}\right)_{(x,y,t)} = 0 \quad (5.33b)$$

And,

$$\theta(x, y, 0) = 30 \quad (5.33c)$$

The exact solution of this example is given by (Han-Taw Chen et al. 1988):

$$\theta(x, y, t) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} B_n \cos\left[\frac{(2i-1)\pi x}{6}\right] \sin\left[\frac{j\pi y}{3}\right] * \exp\left[-\left[\frac{k_x(2i-1)^2\pi^2}{36} + \frac{k_y j^2\pi^2}{9}\right]t\right]$$

Where,

$$B_n = \frac{240}{\pi^2 j(2i+1)} (-1)^{i+j} [(-1)^i - 1]$$

Table 5.1 below shows a comparison of the present numerical solution with the exact solution, and the solutions of references (Han-Taw Chen et al. 1988 and Bruch and Zyvoloski 1974). As one can see the present solution is in very good agreement with the exact solution, and more accurate than those of Bruch and Zyvoloski (1974).

Table 5.1 Solution Corresponding to $t=1.2$ sec

<i>Node position</i>	<i>Present solution</i>	<i>Exact solution</i>	<i>Han-Taw Chen et al. 1988</i>	<i>Bruch and Zyvoloski 1974</i>	<i>Deviation from the exact solution</i>
8	4.989	4.972	4.988	5.107	0.32%
17	6.098	6.077	6.098	6.244	0.34%
31	3.476	3.452	3.464	3.548	0.69%
50	5.078	5.058	5.079	5.206	0.39%
53	2.989	2.973	2.985	3.060	0.53%
55	2.366	2.347	2.360	2.422	0.80%
94	1.997	1.985	1.997	2.050	0.60%
108	0.597	0.593	0.596	0.612	0.67%

5.3.3 Example 3 (Three Dimensional Problem)

In this example the heat dissipation of a solid plate is analyzed. The square plate initially at 10°C , and the temperatures on the boundaries of the solid are kept constant. For simplicity, it is assumed that $\alpha_x=\alpha_y=\alpha_z=1.0\text{ m}^2/\text{sec}$ (α is the thermal diffusivity of the solid). Also $L_x=L_y=L_z=1.0$, and $\Delta x=\Delta y=\Delta z=0.125\text{ m}$. Where, L_x , L_y and L_z are the lengths of the solution domain in the x , y , and z directions, respectively. Thus, the governing equation, boundary conditions, and the initial condition for this example are given by,

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} = \frac{\partial \theta}{\partial t} \quad (5.34)$$

$$\theta(0, y, z, t) = \theta(1, y, z, t) = 0 \quad (5.35a)$$

$$\theta(x,0,z,t) = \theta(x,1,z,t) = 0 \quad (5.35b)$$

$$\theta(x,y,0,t) = \theta(x,y,1,t) = 0 \quad (5.35c)$$

And

$$\theta(x,y,z,0) = 10 \quad (5.35d)$$

The exact solution of this example is given by, (Han-Taw Chen et al. 1988)

$$\theta(x,y,z,t) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} C_{ijk} \sin(i\pi x) \sin(j\pi y) \sin(k\pi z) * \exp\left(-(i^2 + j^2 + k^2)\pi^2 t\right)$$

Where,

$$C_{ijk} = \frac{80}{ijk\pi^3} \left((-1)^i - 1 \right) \left((-1)^j - 1 \right) \left((-1)^k - 1 \right)$$

A comparison of the present solution with the exact solution and the solution of Han-Taw Chen et al. (1988) is shown in Table 5.2. The present solution is in good agreement with the exact solution and also in very good agreement with the traditional numerical method used by Han-Taw Chen et al. (1988). Increasing the number of nodes is expected to make the present solutions converge toward the exact solutions.

Table 5.2 Comparison of the present solutions with exact solutions at $t=0.06$ sec

Node Position (m)	Present Solution	Exact Solution	Han-Taw Chen et al. 1988	Deviation from the exact solution
(0.375,0.25,0.5)	2.24001	2.279	2.241	1.7%
(0.5,0.5,0.5)	3.39249	3.462	3.389	2.0%
(0.75,0.5,0.25)	1.72826	1.751	1.726	1.3%
(0.375,0.375,0.375)	2.69816	2.744	2.695	1.6%

5.3.4 Example 4 (The Current Numerical Technique vs. The PHOENICS Code)

In this example, the accuracy of the current numerical technique will be compared with the predictions from the PHOENICS code solving the same problems. Xudong Yang and Q. Chen (1998) used a Computational Fluid Dynamics (*CFD*) approach to predict the emissions of VOC's from particleboard. They used the PHOENICS code to solve the conservation equations for continuity, momentum, energy and the mass transport. Then the experimental emission data were fit to the solution and the model parameters were estimated ($D=4 \times 10^{-11} \text{ m}^2/\text{sec}$, $k_c=1.0$ and $C_0=1.408 \times 10^{-7} \mu\text{g}/\text{m}^3$). Figure 5.10 illustrates the result obtained by the present model versus the PHOENICS code prediction. As can be seen, the numerical technique employed in this study maintained the same degree of accuracy exhibited by the PHOENICS code.

Figure 5.10 Current model prediction versus the PHOENICS code (the result is scaled by the factor of 1174)

5.4 GENERAL BEHAVIOUR OF THE MODEL

As stated earlier in this thesis the main feature of the current modelling approach is that all the model parameters have well defined physical meanings. Each is either a physical property for the source or for the environment. Furthermore, the physical formulation used here separates the properties for environment (*for example* N, Q, V) from those of the source (*for example* $C_0, D, L, \dots$ etc), so that the impact of each parameter on the emissions from the dry sources can be investigated. This will greatly facilitate product reformulation strategies aimed at preventing indoor air contamination by developing a clear understanding of the factors that control the emission process. In this section the general behavior of the model

is briefly examined. And the influence of the key model parameters such as C_0 , D , k_e , and h on the resulting contaminant concentration in the air is investigated.

5.4.1 The Influence of the Initial Concentration in the source

Figure 5.11 shows the effect of a variation in C_0 , the initial concentration in the source on the resulting contaminant concentration in the chamber air. As shown in the figure the resulting contaminant concentration in the chamber air depends linearly on C_0 , the initial concentration in the source, and that the shape of the chamber concentration as time plot will scale proportionally. This suggests that the most effective way to reduce emissions from indoor sources is to reduce the value of C_0 , the initial concentration of the VOC's in the source.

Figure 5.11 Influence of Initial Concentration in the Source on the Resulting Contamination Concentration in the Chamber Air

5.4.2 The Influence of Diffusion Coefficient

Figure 5.12 illustrates the variation of the chamber contaminant concentration with time at different values of D , the internal diffusion coefficient. The values of D vary between 1.0×10^{-10} and $1.0 \times 10^{-12} \text{ m}^2/\text{sec}$. By comparing the different profiles, it may be concluded that the internal diffusion coefficient has a great influence on the emission rate. Increasing the diffusion coefficient results in a higher emission rate at early times resulting in higher concentration in the gas phase. This will result in more rapid depletion of the contaminant in the source.

Figure 5.12 Influence of Internal Diffusion Coefficient on the Resulting Contamination Concentration in the Chamber Air

5.4.3 The Influence of Partition Coefficient

Figure 5.13 illustrates the variation of the chamber contaminant concentration with time at different values of k_p , the equilibrium partition coefficient. The selected values of k_p vary between 100 and 100000. Increasing the value of the equilibrium partition coefficient decreases the emission rate at early times and results in a much slower depletion rate of source contaminant. However, the influence of a change in k_p is virtually insignificant below a value of about 1000.

Figure 5.13 Influence of Internal Partition Coefficient on the Resulting Contamination Concentration in the Chamber Air

5.4.4 The Influence of Convective Mass Transfer Coefficient

Variation of the chamber contaminant concentration with time at different values of h , the convective mass transfer coefficient is illustrated in Figure 5.14. By comparing the profiles, it is obvious that the boundary layer limitations are unimportant for dry sources. In other words when we are dealing with dry sources, the velocity field and the level of turbulence are immaterial. This conclusion has been confirmed by other researchers (see section 5.2.4.3).

Figure 5.14 Influence of Convective Mass Transfer Coefficient on the Resulting Contamination Concentration in the Chamber Air

5.5 EXPERIMENTAL VALIDATION OF THE PREDICTION MODEL

Three different examples were selected to validate the current modelling approach. In the first example (*Case I*), the model prediction (*using the predetermined model parameters*) was compared with the chamber observation for the particleboard. In the second example (*Case II*) the chamber emission data from the sub-floor (*Recycled Automobile Tires*) was compared with the model prediction. Finally, the third example (*Case III and IV*) was selected to compare the experimental emission data (*from both small and full-scale chamber*) emitted from the composite source (*1/4" plywood // sub-floor // 5/8" plywood*) were compared with the model prediction.

5.5.1 Dry Single Homogenous Sources

5.5.1.1 Case I: Prediction of VOC Emissions from Particleboard

The comparison between the model predictions and the chamber observations are illustrated in Figure 5.15. Careful examination of Figure 5.15 reveals that, the model tends to under predict the early chamber data and over predict the later data. This effect may be attributed to many factors. For instance, it may be attributed to the values of model parameters namely, D and/or k_e (*inaccurate estimation of the model parameters*). The other factor is related to the test procedure itself. For example, placing the test material in a sealed bag prior to testing may have stopped the emission because the vapour concentrations of the emitting VOC at the surface may get very high (*leading to accumulation of the pollutant on the surface of the solid*). This may imply an almost

homogenous concentration in the particleboard at test start, resulting in a strong initial emission. Therefore, this initial period (*evaporative control period*) cannot be well predicted by the diffusion model. Another factor that may have caused this deviation are the values of the adsorption/desorption coefficients (k_a and k_d). Although the sink effect in the chamber wall is taken into consideration, the values of the adsorption/desorption coefficients (k_a and k_d) used in the model may need to be refined (*the values of the adsorption/desorption coefficients (k_a and k_d) used in the model is based on the work of An, et. al. (1998)*). This could be the reason that the predictions do not agree more fully with the measured data. Probably more effort is needed for characterizing the sink effect. However, an ability to determine model parameters directly, without using chamber data, will avoid the extra complexity and probably provide a more reliable measure of the model parameters. In general, the agreement between the model prediction and the chamber data is reasonable considering the ± 10 to 15% uncertainties involved in the tube sampling method.

Figure 5.15 Model Prediction vs. the Chamber Observations for the Two Compounds

5.5.1.2 Case II: Prediction of VOC Emissions from Sub-Floor Tile (Recycled Automobiles Tires)

Figure 5.16 below, illustrates the comparison between the model predictions and the chamber observations for the three VOC species. The correspondence between predicted and measured concentrations is relatively good. Again the high initial chamber concentration in the early time cannot be predicted by the diffusion based model. Poorer correspondence for the p-xylene (*the model seems to under estimate the chamber concentration*) may be due to the inaccurate estimation of the value of C_0 (*initial concentration in the source*).

Figure 5.16 Model prediction vs. the chamber observations for the three compounds

5.5.2 Composite Sources

5.5.2.1 Case III: Prediction of VOC Emissions from Material System in the Small – Scale Chamber

A photograph of the material system tested in the small chamber is shown in Figure 4.11. The sub-floor tile (*the main sources of VOCs*) is sandwiched above and underneath by low-permeability, zero-concentration 1/4" and 5/8" plywood layers. The configuration shown simulates the real case scenario of the material system used indoors (*part of floor*). The comparison between the model prediction and the small-scale chamber observation for the three selected species is shown in Figure 5.17.

An inspection of Figure 5.17 reveals that there are a difference between the predicted and the observed chamber concentration profiles. This unexpected variability in emission profile may have resulted from the VOC's leakage at the materials interface (*imperfect contact between the sub-floor tile and the plywood layers*), since it is easier for the pollutants to leak through the interface gap than to diffuse through the plywood layers. This discrepancy is despite the fact that many precautions were taken to eliminate VOC's leakage at the interface, such as using many nails to fasten the materials together. Test results obtained with the material system using the specimen holder shown in Figure 4.15 support the hypothesis that the imperfect contacts (*pollutant leakage at the interface*) significantly effect the model prediction. As will be shown later, the presence of the specimen holder improved the correspondence between predicted and measured concentrations. Also, the estimated values of C_0 may have contributed to this variability in the emission profile (*the measurements for C_{bag} have a precision of about $\pm 10\%$ which is reflected in the calculated values for C_0*).

Figure 5.17 Model Prediction vs. the Chamber Observations for the Material System in the Small-Scale Chamber

The concentration gradients of benzene at different time intervals (50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 h) through the material system are shown in Figure 5.18. As can be seen from the figure, in the early time the concentration gradients through both layers (1/4" and 5/8" plywood) increase causing the concentration in the chamber air to increase (*charging period*). It therefore takes some time for the concentration front propagated by the high concentration layer (*Sub-floor Tile*) to reach the surfaces. As time elapses the concentration gradient in the materials system gradually decreases. After about 500 hours, more than 50% of the benzene has been emitted and the concentration

gradient within the sub-floor becomes almost flat. This reduction in the concentration is responsible for the semi-constant chamber concentration at the later time.

Figure 5.18 Concentration Distribution Curves within the Materials system

5.5.2.2 Case IV: Prediction of VOC Emissions from Material System in the Full- Scale Chamber

The materials system described above (1/4" plywood // Sub-floor Tile // 5/8" plywood) was scaled-up and tested in the full-scale chamber. The comparison between the model prediction versus the full-scale chamber observation for the three selected species is shown in Figure 5.19. Poorer correspondence of the compounds predicted (*the model seems to under estimate the chamber concentration*) is attributed to the same problem

observed in the small-scale chamber namely, the leakage of the pollutants at the interface. Unlike the small-scale chamber case, the materials system test in the full-scale chamber is relatively big which has made it even more difficult to maintain perfect contact at the materials interfaces, which is reflected in the observed chamber concentration. More modelling effort is needed to account for the imperfect contact at the materials system interfaces a factor that is not built into the mathematical model.

Figure 5.19 Model prediction vs. the chamber observations for the material system in the full-scale chamber

5.5.2.3 Results of the Material System Using the Specimen Holder

The main purpose of this sub-section is to investigate the effect of the interface leakage assumed above on the model prediction. In the current case, the stainless steel holder (See *Figure 4.15*) was used to hold the materials assembly (*1/4" plywood // Sub-floor Tile*) so

that only the test surface of the specimen is exposed to the air (*this will eliminate the uncertainty associated with the edges*). Then the materials system was tested in the small-scale chamber. The model prediction versus chamber observation for the materials system with specimen holder is shown in Figure 5.20. As can be seen from the comparison (with Fig 5.12) the presence of the specimen holder improved the model prediction. This supports the hypothesis stated earlier that the leakage at the materials interfaces is the main cause of the poor correspondence between the predicted and the observed chamber concentration specially in the full-scale chamber.

Figure 5.20 Model prediction vs. the chamber observations for the material system with specimen holder in the small-scale chamber

Chapter VI

DEVELOPMENT AND VALIDATION OF A PREDICTION MODEL FOR COMPLEX SOURCES

6.1 INTRODUCTION

In this chapter, a mass transfer based model for predicting the emissions from a composite system (*Tile // Glue // Substrate*) is presented. It was clear that the emission model should contain four mass transfer parameters (*Diffusion coefficient D , Initial concentration C_0 , partition coefficient k_p and Convective mass transfer coefficient h*). In chapter III the method and procedure developed for independent determination of diffusion and partition coefficients (D , and k_p respectively) of the solid building materials (*Note that C_0 can be determined by using the equilibrium headspace and the partition coefficient k_p*) is described. However, in order to describe the emissions from a composite system containing a complex source, the diffusion coefficient through the glue (*complex source*), and the convective mass transfer coefficient h still need to be determined. Two counteracting

effects occur during the early stages of outgassing from the glue or any other complex source. First there is a tendency for volatiles to escape rapidly, since there is little resistance to their escape; secondly, there is a build-up of a surface skin (*at varying speeds depending on the type of adhesives*) which presents a growing resistance to the escape of the volatiles. This change in phase (*Drying process*) causes the physical properties of the glue such as the diffusion coefficient to change with time. Therefore, it is useful to establish an understanding of how a volatile material moves through complex sources (*i.e. Glue, Sealant, Caulks, ...*) and is then given off into the surrounding air space.

The first part of this chapter describes a simple working hypothesis, which gives a fairly good account of how the volatile material moves through adhesives. Then, based on this hypothesis, the attempt and the major obstacles to modelling the emission from the glue are discussed. Finally, the rest of the chapter is devoted to describing the development of the method used to determine the diffusion coefficient of the adhesive as a function of time. Also some preliminary results from the model prediction for the system assembly (*vinyl tile // adhesive*) are presented.

6.2 DISCUSSION OF VOLATILE TRANSPORT

A complex source, such as an adhesive, generally consists of a mixture of solids, liquids and gases. The solid component can be regarded as a rigid matrix, containing voids that are occupied by a mixture of liquids and gases. The liquids are mainly of a volatile nature and the gases are their gaseous phase.

In a newly-applied glue surface, the volatiles at the surface, or in the voids very close to the surface, will evaporate and escape. During this initial period of emission, the glue will also experience other physical change (*change in phase*), of which the most important is the formation of a surface skin. Thus, two counteracting effects occur during the early stages of outgassing: first there is a tendency for volatiles to escape rapidly, since there is little resistance to their escape; secondly, there is a build-up of a surface skin (*at varying speeds depending on the type of adhesives*) which presents a growing resistance to the escape of the volatiles.

At the end of this initial stage, it can then be assumed that the adhesive has formed a resistive skin, and the voids close to the surface are totally depleted (*i.e. contain no volatiles in liquid form*). Deeper within the glue, the volatiles still exist in liquid form and will have a free surface at which evaporation will occur. The evaporated volatile then has two obstacles: first it must diffuse through the depleted voids, then, at the surface, it must diffuse through the more resistive skin. As the outgassing progresses, the remaining gaseous volatiles will have to diffuse through an increasingly longer path in their movement to the glue surface.

The general emission profile should therefore consist of a high initial emission rate, decreasing very rapidly as the skin forms. The overall result is a gradually decreasing emission rate due to the lengthening diffusion path.

The rate of air movement over the adhesive surface (*or any complex sources*) plays an important part at least in the early stage of the emission process described. If the air is stagnant then the airborne concentration of emitted volatiles (*close to the surface*) will increase relatively quickly and this high local concentration will inhibit the escape of further volatiles. Conversely, if the glue surface is swept by a continuous air movement, then the air close to the surface will have a low volatile content and there will be little resistance to outgassing. At any instant of time, the rate of emission is therefore dictated mainly by three resistances: the resistance to movement through the voids, the resistance to movement through the surface skin and the resistance to movement in the air space, which is termed boundary layer resistance. The emission profile, namely the variation of emission rate with time, is dictated by the relative values of these three resistances and the way in which they change throughout the emission period.

From the above discussion one can conclude that, due to the phase change within the adhesive with time, the diffusion coefficient of the VOCs through the adhesive, for example, is not constant (*and hence, the resistance is not constant*). Therefore it is necessary to find a method to calculate D (*diffusion coefficient*) in the adhesive layer as a function of time (*as the glue is drying*).

6.3 A MATHEMATICAL DESCRIPTION OF GLUE FILM DRYING BY SOLVENT EVAPORATION

Figure 6.1 Mathematical modelling of complex sources

In this mathematical description the glue matrix is regarded as a "reservoir" containing the volatiles in liquid form. With progressive outgassing of the volatiles, the level of the reservoir falls, and is represented at any instant by the depletion depth " x ". Thus, during the emission process, the gaseous volatiles must diffuse through an ever increasing distance to the surface. Eventually, within a finite time, the reservoir will become totally depleted, and at that point, the emission processes will be terminated sharply. In fact, when the liquid volatile is totally depleted, the voids will still remain filled with gaseous volatile and the emission process will continue but with very low rates (*long term phenomena*).

The rate of emission is related to the rate of drop of the reservoir level as follows
(neglecting the mass of the VOC's in the depleted zone):

$$R = C_0 \frac{dx}{dt} \quad (6.1)$$

Where:

R = emission rate per unit area ($mg/m^2/hr$)

C_0 = concentration of liquid volatile in the glue (mg/m^3)

d = Total thickness of the glue (m)

x = depletion depth (m)

t = time (hr)

For diffusion through the glue (*depleted zone*) it is assumed that:

$$R = \frac{D_g}{x} (C_s - C_g) \quad (6.2)$$

Where:

D_g = is the effective diffusivity of VOC through the depleted zone (m^2/hr)

C_s = Concentration of gaseous volatile at the glue surface (mg/m^3)

C_g = Concentration of volatile under saturated conditions (mg/m^3)

Also at the glue surface interfacing with the air we have (*convective boundary*)

$$R = h(C_g - Y) \quad (6.3)$$

Where:

h = is the convective mass transfer co-efficient (m/hr)

Y = Concentration of the volatile of interest in the air space above the glue (mg/m^3)

The variable C_s can be eliminated by combining Equations (6.2) and (6.3), then the three equations can be reduced to:

$$R = \frac{h(C_s - Y)}{(1.0 + hx / D_e)} = C_o \frac{dx}{dt} \quad (6.4)$$

In general it is suggested that two regimes can be considered. The first is an initial emission rate regime, probably of very short duration (*less than two hours*), in which the emission rate is controlled by aerodynamic conditions (*such as air velocity, level of turbulence, and the air change per hour*). The second is a longer-term emission rate regime which is controlled by the internal diffusion process, beginning when the rate of diffusion to the surface is just balanced by the rate of convective mass removal from the surface, which is typically a few hours after application of the glue and continues up to the end of the emission process. Between these two regimes there must be a transition regime in which both internal diffusion and convective mass transfer process are influential. The transient regime is given by the full expression in Eq. (6.4), in this regime it is likely that the surface skin is still growing, and the effective diffusion coefficient will therefore decrease rapidly as the skin forms. The next two subsections will discuss the two aforementioned regimes in detail.

6.3.1 Convective Regime

During the early stages of the skin formation process the resistance offered by the skin is small and the effective diffusion coefficient of the glue will be relatively high. Also, since the emission process is at an early stage, the depletion depth “ x ” will be relatively small. It can be shown that; *(The order of magnitudes of convective resistance vs. diffusive resistance)*

$$hx/D_g \ll 1.0$$

So from Equation (6.4) we get:

$$R = h (C_s - Y) \quad (6.5)$$

Under these conditions the mass transfer coefficient “ h ” has a dominant effect on emission rate. This coefficient is related to the air movement conditions above the surface, the rate of air movement will determine the value of convective mass transfer coefficient, which in turn will determine the emission rate as given by equation (6.5). This is consistent with the results of many laboratories, when they study the emission from wet materials.

6.3.2 Diffusion Controlled Regime

After the initial skinning period the effective diffusion coefficient will be relatively small. Therefore, it is reasonable to assume that;

$$h\sqrt{D} \gg 1.0$$

and by using Eq (6.4)

$$\frac{dx}{dt} = -\frac{D_g}{x} \frac{C_s - C_0}{C_0}$$

After separating the variables, and integrating we get

$$x = \left(\frac{2D_g C_s}{C_0} \right)^{0.5} t^{0.5} \quad (6.6)$$

The depletion depth x is directly proportional to the mass loss from the glue. So, when the emission process is dominated by internal diffusion through the glue, the mass loss, varies as the square root of time.

So, from Eqs. (6.1 and 6.6) we get:

$$R = \left(\frac{D_g C_s - C_0}{2t} \right)^{0.5} \quad (6.7)$$

It should be pointed out that, although the immediate objective of such formulations is to gain some insight into the drying (*curing*) process of the complex sources, the ultimate goal is to relate the emission data to some mass transfer parameters such as h , D_g , C_{sat} , so

that a mass transfer based model can be developed to predict the impact of the emission of these materials on indoor air quality. The next subsection will discuss the first attempt to analysis the emission data from a small environmental chamber, in order to determine h , D , and C_i .

6.3.3 The First Attempt to Analysis of the Emission Data from the Floor Adhesive

Theoretically, based on the preceding discussion and Equation (6.5) one can conclude that, if the data from the early emission period is used (*less than one hour*), one can determine the value of " h ", and " C_i ". And, then the value of D will be extracted. The first step is to fit the emission *data (early period)* to the convective regime equation Eq. (6.5). From the mass balance around the test chamber we have,

$$V(dY/dt) = AR - QY \quad (6.8)$$

or

$$dY/dt = (A/V) R - (Q/V) Y$$

Since

$(A/V) = L$ "chamber loading factor" (m^3) and

$(Q/V) = N$ "Air exchange" (hr^{-1}) then;

$$dY/dt = L R - N Y \quad (6.8a)$$

sub. Eq. (6.5) into Eq. (6.8a) we get:

$$dY/dt = Lh C_i - Y(Lh + N) \quad (6.9)$$

if we assume $(Lh + N) = \alpha$, and $(Lh C_i) = \beta$ then the exact solution of the above differential equation is;

$$Y = \beta / \alpha \{1.0 - \exp(-\alpha t)\} \quad (6.10)$$

In which “ h ” and C_i are contained in the parameters α and β . Hence by fitting this equation (Eq. 6.10) to the chamber data in the convective regime the values of α and β can be determined and the values of both “ h ” and “ C_i ” extracted. Note that, Eq. (6.10) is a curve rising exponentially from zero to an asymptotic value (β/α).

Upon fitting Eq. (6.10), the values of “ h ” can be determined at any velocity and hence a correlation between “ h ” and velocities can be determined.

Though plausible in principle, this approach fails in practice. The reason can be explained with reference to Figure 4.17, which gives the concentration variations from the glue surface with time. Again Eq. (6.10) is a curve rising exponentially from zero to an asymptotic value (β/α). In Figure (4.17) it is obvious that the experimental data do not give adequate coverage of the regime, even though the air sampling rate was designed to stretch this initial part of the curve. Even if the first three data points are used it is questionable whether they belong to the initial regime or the transient regime (*Where Eq. (6.10) is no longer valid*).

It should be pointed out that, the value of “ C_1 ” (*Concentration at standard vapour pressure* [$C_1 \neq C_{saturation}$]) is treated as an unknown quantity due to the nature of the surface itself. The definition of saturated vapour pressure contains an element that is often overlooked: it applies to an extensive, flat liquid surface in equilibrium with the airspace above it. Such conditions do not apply to a liquid inside a glue matrix, presumed to consist of very small, interconnected voids. In general, the saturated vapour pressure depends partly on the configuration of the liquid/Gas interface. The effect can be represented in terms of the *Knudson Number*, which is the ratio of molecular mean free path to the “Characteristic dimension” of the interface. For an extended flat surface this characteristic dimension is infinite, so the *Knudson Number* is zero, and the surface configuration has no moderating effect on the saturated vapour pressure. But, for a liquid compound within a glue void, the characteristic dimension is the diameter of the void, which is probably of micron size and is therefore of approximately the same magnitude as the molecular mean free path. As a result the *Knudson Number* will be relatively large and will have a significant effect on the saturated vapour pressure as used in the above mathematical development. Therefore, the true saturated vapour pressure inside the glue void will differ from the conventional value, though by what amount it is impossible to say without considerable study and experimentation.

Therefore, the diffusion coefficient D , through the glue as well as the convective mass transfer coefficient h over the glue surface cannot be determined from the above approach because it is difficult (*if not impossible*) to tell when the convective regime ends and the

transient regime starts. Another alternative to determining the value of D as a function of time, is to use the measured emission data and the transient diffusion equation with variable diffusion coefficient $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial C}{\partial x})$. So by fitting the emission data to the transient diffusion equation the relationship between the diffusion coefficient and the concentration (*and hence the time*) can be determined. More details about this approach will be discussed in the next section.

6.4 THE METHOD USED TO ESTIMATE D AS A FUNCTION OF TIME

In the current approach, the one-dimensional transient diffusion equation is fitted to the experimental emission data from the glue. From Fick's First Law we have

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial C}{\partial x}) \quad (6.10)$$

The first boundary condition (the convective surface)

As illustrated in the figure 6.2 below, the stainless steel glue container is used to control the amount of glue applied (*the application procedure is described elsewhere Xiangdong, Li (1997).*

Figure 6.2 Schematic representation of the glue in the stainless steel container

$$\left(\frac{\partial C}{\partial x}\right)_{x=L} = \left[\frac{-hNC_s}{k_e D(Lh + N)} \right] - \left[\frac{h}{k_e D(Lh + N)} \right] \left(\frac{\partial C}{\partial t}\right)_{x=L} - \left[\frac{1}{(Lh + N)} \right] \frac{\partial}{\partial t} \left(\frac{\partial C}{\partial x}\right)_{x=L} \quad (6.11)$$

The convective boundary condition (Equation 6.11) is obtained by the same method described in chapter V where,

k_e is the equilibrium partition coefficient (*dimensionless*)

h is the convective mass transfer coefficient, (m/hr)

C_s is the concentration at the surface of the source (mg/m^3)

$L=AV$ is the chamber loading factor (m^3)

$N=Q/V$ is the chamber air exchange rate (hr^{-1})

The second boundary condition (the impervious surface)

Since the stainless steel container was used, the second boundary condition at $x=0$ is,

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = 0 \quad (6.12)$$

The initial condition

$$C(x,0) = C_0 \quad (6.13)$$

The diffusion coefficient D is assumed to change with the concentration C according to the following equation,

$$D = D_0 \left[\frac{C}{C_0} \right]^2 + D_{dry} \left[1 - \left(\frac{C}{C_0} \right)^2 \right] \quad (6.14)$$

Where;

C_0 is the initial concentration of the VOC in the glue (mg/m^3)

D_0 is the initial diffusion coefficient (m^2/sec)

D_{dry} is the diffusion coefficient of the VOC through a completely dried glue (m^2/sec)

C is the concentration at any time " t " (mg/m^3)

As stated earlier in order to control the amount of the glue applied and to reduce the uncertainty associated with the edges, the glue was applied in the stainless steel container following the same procedure described by Xiangdong Li (1997). The application procedure is summarized in chapter IV.

The numerical method described in chapter V was used to solve the above equation (Eqs. 6.10, 6.11, 6.12, and 6.13). And the experimental chamber data (*generated in chapter IV*) was fitted to the solution to determine the coefficient D_0 . Two important notes should be mentioned here regarding the values of h (*the convective mass transfer coefficient*) and C_0

(the initial concentration in the adhesive layer). The convective mass transfer coefficient h is determined by using a correlation developed by Spark et. al (1996). The correlation gives a relationship between three mass transfer parameters namely; the Reynolds number (Re), Schmidt Number (Sc), and Sherwood Number (Sh). The velocity over the adhesive surface was measured using a hot wire anemometer. The diffusivity of the decane in air ($0.02 \text{ m}^2/\text{hr}$) was used as a representative of the diffusivity of all compounds. The square root of the glue surface area was used as a characteristic length for calculating the value of the Reynolds number. The value of W (the initial amount of VOC in the adhesive applied) was estimated by conducting a long-term emission test (800 hr) and then integrating the concentration curve.

$$W = \frac{Q}{2} \sum_{i=1}^{n+1} ((C_i + C_{i+1})(t_{i+1} - t_i))$$

Where

Q = Air exchange flow rate (m^3/hr)

C = Chamber concentration of a given compound (mg/m^3)

t = Time (hr)

n = Total number of data points

It should be pointed out that in order to reduce the number of unknowns involved in the curve fitting the value of the diffusion coefficient of the VOC through the complete dried glue D_{dry} was determined independently. The value of the diffusion coefficient D_{dry} of the VOC through the completely dried glue was determined by using the diffusimetric apparatus described in chapter III. The glue sample was prepared by applying the glue in

the 1 mm container by using the application method described above. After being cured (it takes about 2 months) the glue slab was extracted and cut into circular specimens (80 mm in diameter), and placed on a glass substrate in an environmentally controlled room with a clean air supply for more than one year before testing. This aging period is very important in order to allow the VOCs remaining in the specimens to be minimal and the specimen to be in equilibrium with the test condition.

The following steps will summarize the method used to estimate the value of the diffusion coefficient of the glue as a function of time.

- (1) A sample of completely dried adhesive was prepared and tested after one year by using a diffusimetric apparatus. Then the values of the diffusion coefficient of the VOC through the completely dried glue D_{dr} and the equilibrium partition coefficient k_e were determined.
- (2) The method described by Xiangdong Li (1997) was used to apply the adhesive in the stainless steel container. Then the value of C_0 was determined by conducting a long-term emission test (800 hr).
- (3) The convective mass transfer coefficient h was determined by using a correlation developed by Spark et. al (1996).
- (4) The numerical method described in chapter V was used to solve the transient diffusion equation (Eq. 6.10), and the experimental chamber data (generated in chapter IV) was fit to the solution to determine the coefficient D_0 (note that only one unknown is involved in the curve fitting process).

6.5 RESULTS FROM THE ADHESIVE

The first part of this section deals with the result from the adhesive alone (*free surface*). The results of the diffusion coefficient variation are shown, and the values of the parameters D_0 and D_{drv} are presented. In the second part of this section the model prediction versus the small-scale chamber observations for the complex systems assembly (*vinyl // adhesive assembly*) are discussed.

6.5.1 Variation of Diffusion Coefficient With Time

The resulting form of the diffusion coefficient variation is shown in Figures 6.3, 6.4, and 6.5 for nonane, decane, and undecane respectively. The parameter values (D_0 and D_{drv}) for the selected compounds are given in Table 6.1. Two characteristics of Figure 6.3 deserve some discussions. First, over the first two hours the value of the diffusion coefficient falls rapidly from a high value to a very low one. This can be attributed to the formation of a surface skin, which offers increasing resistance to volatile movement and thereby reduces the effective diffusion coefficient D . Once this initial skin formation transient has ended, the coefficient displays a slow and steady decrease with time. Second, the diffusion coefficient at the surface compartment ($x = 0.1 \text{ mm}$) falls very rapidly compared with the diffusion coefficient at other locations deeper in the container. As the time elapses the depleted front propagates deeper into the glue film and the diffusion coefficients at the different locations slowly approach the constant value (D_{drv}).

Figure 6.3 Variation of diffusion coefficient with time for nonane (Numerical solution of the Transient diffusion equation with variable diffusivity)

Figure 6.4 Variation of diffusion coefficient with time for decane (Numerical solution of the Transient diffusion equation with variable diffusivity)

Figure 6.5 Variation of diffusion coefficient with time for undecane (Numerical solution of the Transient diffusion equation with variable diffusivity)

Table 6.1 Parameters for the Adhesive

Compound Name	D_0 (m^2/sec)	D_{dry} (m^2/sec)
Nonane	7.02×10^{-10}	7.25×10^{-12}
Decane	2.92×10^{-10}	8.92×10^{-13}
Undecane	1.78×10^{-10}	7.08×10^{-13}

6.5.2 Emission from the Complex Systems Assembly

The emission data from the system assembly (vinyl tile // adhesive generated in chapter IV) are interpreted using the diffusion based model (the diffusion model described in chapter V) with variable diffusion coefficient through the adhesive (all the model

parameters are determined independently). As shown in Figure 6.6 the diffusion model appears to fit the data well, supporting the notion that the emission rate is governed by internal diffusion through the system assembly.

Figure 6.6 Model predictions versus chamber data for the system assembly

Chapter VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The main objective of this study was to develop a mass transfer theory based model to predict the emission rates from dry sources as a function of time and environmental parameters. The uniqueness of the new modelling approach is that the key parameters for the model (D , C_0 , and k_e) were determined independently. The modelling approach has been applied to two single dry sources (*particleboard and sub-floor tile*) and a materials system assembly (*1/4" plywood // sub-floor tile // 5/8 plywood*). In addition, a model has also been developed to describe the emissions from a complex source (*floor adhesive*) and a system containing a complex source (*adhesive // vinyl floor tile*)

Substantially, the objectives have been achieved. The modelling approach has been taken to the point where they will serve as a foundation for future work, though further refinement will be needed before the techniques can be translated into definitive standard procedures. The experiments conducted have made possible a fairly comprehensive

assessment of the developed modelling approach, and have given clear indications on the need for further development and refinement. The major findings from the present study are summarized as follows:

7.1.1 Regarding the Headspace Analysis

- (i) The results of the headspace analysis show that the floor adhesives are a potential emitter (*source*) of VOCs in indoor air. The TVOC concentration of the floor adhesive is much higher than the TVOC concentration of any dry sources tested in this research.
- (ii) The main compounds identified in the headspace analysis from the sub-floor tile (*recycled tires*) were benzene, toluene, and p-xylene. Two of these compounds namely benzene and toluene are classified as human carcinogens.
- (iii) The main compounds identified in the headspace analysis from the engineered wood products (*OSB, plywood, and particleboard*) were classified by compound chemical class. Aldehydes and Terpenes were the main compounds identified in the headspace screening.
- (iv) The main compounds identified in the headspace analysis from the floor adhesive were mainly aliphatic hydrocarbons, which ranged from C_8 to C_{12} , and C_2 to C_5 cyclohexane derivatives.

7.1.2 Regarding the Diffusion Measurement Procedure

- (i) The experimental results show that the measured values of the diffusion and partition coefficients (D , and k_p) of the selected materials behave in fashions that

are consistent with the physical properties of the compounds. Consistent with the results reported from the previous studies, it was found that the values of diffusion coefficients for a given material are inversely proportional to the molecular weights of the VOCs, whereas the value of the partition coefficients are proportional to the vapour pressures of the VOCs. Therefore, both the type of the materials and the chemo-physical properties of the compound affect the results.

- (ii) It was found that the variation of the diffusion coefficient with the molecular weight for the carpet does not follow the same trend as the other dry product test in this study. This deviation may be attributed to the nature of the carpet surface.
- (iii) Chemical isomers, namely compounds with similar molecular weights and chemical composition but different molecular structures, can have different diffusion and partition coefficients.
- (iv) Based on the error analysis presented in chapter III, a significant improvement in the accuracy of the measured quantities (D , and k_p) can be achieved by improving the measurements in the values of c_{a1} and c_2 (*the main source of uncertainty comes from the analytical method*)
- (v) Although the study has focussed on some products, it is felt that the procedures and knowledge base can be broadened to include other products in domestic use. If this is done, it will provide the hard data that is needed for the material emissions database now being developed by the NRC/IRC.

7.1.3 Regarding the Modelling Approach

- (i) The emissions of VOC from dry materials can be well described with the help of the internal diffusion equation. The results shows that, the compartment model is, an excellent prediction tool to account for the simultaneous effect on the emission rate caused by internal diffusion, vapour pressure in the air and the resistance to mass transfer in a gas film above the material.
- (ii) The behaviour of a source that is controlled by internal diffusion is largely independent of the chamber conditions that are typically found indoors. So the prediction of the diffusion controlled source/sink behaviour of indoor materials is possible based only on knowledge of the pre-determined properties of the relevant VOC and the indoor material.
- (iii) The model simulation shows that the resulting contaminant concentration in the chamber air depends linearly on C_{i0} , the initial concentration in the source, and that the shape of the chamber concentration will scale proportionally. This suggests that a effective way to reduce emissions from indoor sources is to reduce the value of C_{i0} , the initial concentration of the VOCs in the source.
- (iv) The internal diffusion coefficient has a great influence on the emission rate. Increasing the diffusion coefficient results in a higher emission rate at early times and more rapid depletion of the contaminant in the source.
- (v) Increasing the value of equilibrium partition coefficient decreases the emission rate at early times and results in much slower depletion rate of source contaminant. However, the influence of a change in k_p is virtually insignificant if k_p is less than about 1000.

- (vi) The boundary layer limitations are unimportant for dry sources. In other words when we are dealing with dry sources, the velocity field and the level of turbulence are immaterial.
- (vii) The presence of an extra resistance on the top of the main source (*vinyl tile // glue or plywood // sub-floor Tile*) significantly reduced the peak emission rates. However, the emission rates from the materials system remained higher after a period of time (approximately 60 days for the plywood //sub-floor tile case, than for the main source alone).
- (viii) The TVOCs from the materials system (*vinyl tile // glue*) are primarily dominated by emissions from the glue component.
- (ix) In general, the predicted results are in good agreement with the experimental chamber data except for cases where edge effect was significant in the experiments.
- (x) The double peaks phenomena displayed by the adhesive emission profiles may be due to the build up of the pollutant vapour pressure behind the skin. This build up of the vapour pressure continues until the pressure is sufficient to open up an escape path, possibly by creating micro-fractures in the skin.
- (xi) The results of this study indicate that the approach involving measuring the key parameters directly proves fruitful for a wide range of dry materials, especially if correlation equations are developed that are based on readily available physical properties of the pollutants. With these independently determined parameters

available, chamber studies could then best be used as a means to verify the reliability of the fundamental diffusion models.

7.2 RECOMMENDATIONS

Based on the results from this study, the following recommendations can be made:

7.2.1 Recommendations Regarding the Diffusion Measurement Procedure

- (i) In order to improve the accuracy of the determination of the equilibrium partition coefficient k_p , bigger test specimen surface areas are desired (*for example use specimen diameter 120 mm instead of 60 mm*). Increasing the specimen surface area will increase the value u (the intercept Eq. 3.20).
- (ii) Special attention should be given to the quantification method especially to the values of c_0 and c_2 .
- (iii) More data are necessary to obtain more accurate correlations between the diffusion and partition coefficients (D , and k_p) and the chemico-physical properties of the pollutants.
- (iv) More materials need to be tested to provide data of internal diffusion coefficients and partition coefficients for more building materials.

7.2.2 Recommendations Regarding the Modelling Approach

- (i) The drawback of this model is that perfect contact is assumed at the material interfaces. Further refinements of the mathematical formulation are needed in order to account for the leakage of the VOCs at the material interfaces.

- (ii) Further research is needed to improve the understanding of the behaviour of indoor sinks with respect to vapour phase organic compounds. Specifically, examination of the behaviour of sinks exposed to dynamic, non-steady source emissions.
- (iii) More information about exposure effect relationships are needed for a range of VOC mixtures. Specifically, the possible long term health effects of complex mixtures of volatile organic compounds at the levels observed in indoor environments. Carefully designed epidemiological studies are required to clarify the role of VOCs for health and comfort of building occupants.

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APPENDIX-A

EQUIPMENT AND TEST FACILITIES

A.1 SMALL SCALE CHAMBER

A.1.1 Overall Small Chamber Description

A 0.4 m^3 stainless steel chamber ($1.0 \times 0.8 \times 0.5\text{ m}$) built at the National Research Council (NRC) of Canada was used to test the emission from all specimens. A schematic diagram of the main measurement system components and the test chamber are shown in Figure A.1 and A.2 respectively. The outer chamber, which housed the inner chamber, was located in a room with a constant temperature ($23 \pm 0.5^\circ\text{C}$). The outer chamber has a top plate, which was screwed down to the body of the chamber. To prevent leakage, Teflon is used as a gasket between the chamber's body and the top plate. This plate has attachments for the air exhaust, the clean air supply unit, the anemometer tube, and the pressure line. Temperature and humidity sensors are located inside the outer chamber to provide the feed back signals directly to the controller. This will maintain the temperature and humidity of the supply air to the outer chamber and the ambient room air temperature at the desired values. As Figure A.3 shows, the outer chamber is equipped with glass front door for fast loading the test specimen in the inner chamber. The inner chamber housed the specimen (*with the specimen holder*). The inner chamber was used to control the velocity and turbulence level over the

Figure A.1 Schematic of the Outer and Inner Chamber Assembly

Figure A.2 Schematic of the Small Chamber Test System

material surface. The velocity over the specimen surface is controlled via A Maxon Servo-Motor equipped by a Teflon fan. The Maxon Servo-Motor rated for maximum 25 volts was used to control the fan speed and thus the air speed across the test specimen. The inner chamber had screened attachments at the air inlet and outlet to provide uniform air flow and to create several levels of turbulence. Two parallel fine mesh screens spaced 20 mm apart were used for a low turbulence flow. All the components including the duct, fan blades, shaft, and stands for the inner chamber are made of stainless steel. In order to avoid introducing contamination from the motor, the fan's D.C. motor was mounted outside the outer chamber. Before the emission test, the air flow characteristics over the material specimen were measured. The velocity across the specimen was measured with a TSI hot-wire anemometer which was placed above the mid-point location of the specimen and 4 cm above the test surface.

The chamber was cleaned and purged with clean air for a minimum of 24 hours before each test. The background contamination of the chamber was examined after 24 hr of flushing at 1 air change per hour using the air purified by the catalytic oxidizer. Air was pumped through the sorption tube at 200 ml/min for 30 minutes. The TVOC concentration in the chamber air was below 0.01 mg/m³.

The complete test facility was located in the (3.5x2.5x2.5 m) test room. The temperature and the relative humidity of the test room was controlled within ± 2 °C and $\pm 5\%$ respectively. An air conditioning unit, which is separate from the rest of the building independently controls both the temperature and relative humidity of the test room. The temperature and relative humidity inside the test room were controlled via a Nortec air

conditioning unit, and humidification unit. All the air conditioning unit components are located outside the test room (*the evaporator, the compressor, and the condenser are located in the ceiling of the building*). Meanwhile, the humidification unit components (*the heater, the fan, the water sink, and the sensors*) are located inside the test room. The humidifier is supplied with distilled water. If the relative humidity in the test room is dropped to a certain value the heater will turn-on automatically, and the fan will blow the vapor into the test room. The temperature and the relative humidity of the test room can be controlled by means of knobs located inside the test room.

Figure A.3 Small Scale chamber

A.1.2 Small Chamber Air Supply Unit

When monitoring the VOC's emissions in the range most commonly encountered in indoor air quality studies, (*i.e. 1 to 5 ppm*), it is necessary to have available a zero air of 0.01 ppm or less contamination. In addition, to the contamination level requirement in the supply air, the temperature, relative humidity, and the flow rate of the zero air should also be precisely controlled. Therefore the outdoor air should be treated in order to meet the above requirements. The following subsections will be devoted to describing the devices which were utilized to precisely control the quality and quantity of the air entering the test chamber (*namely, the Dehumidifier, the Catalytic Oxidizer and the Environmental controller*).

Dehumidifier

Before the outdoor air is introduced into the test chamber, it is first compressed to 300 *kpa* by using an oil-free compressor. The compression unit consists of a high pressure stainless steel vessel and an air pump, which turn on and off automatically by sensing the pressure inside the vessel. Two desiccant dehumidifier columns were used to dry the outdoor air. A clean air supply (*filtered, regulated compressed air at least 20% relative humidity below desired humidity for test procedure*) is necessary. A dirty air supply can cause air controllers to malfunction. These two columns, operate in alternate fashion so that one column is always ready to work.

Figure A.4 Dehumidifiers and Oxidizer System

Catalytic Oxidizer

After the dehumidification process, the compressed dry air enters the Catalytic Oxidizer. In this stage almost 99% of the organic pollutants are removed. The MSA Catalytic Oxidizer, Figure A.4, is a relatively simple, compact, ambient air purifier which can replace the high priced and bulky cylinders to provide zero air that meets indoor air quality contamination requirement levels and purposes. Two-catalyst beds are utilized, each contained within a metal tube. The tubes are connected in series and suspended vertically within a metal housing. An 8 ft length of stainless steel tubing coiled tightly around the inlet side catalyst tube serves to pre-heat the incoming dry air (*The dry air is heated to 350 °C*).

Environmental Controller

The preparation of controlled test atmospheres is an important task in the field of indoor air pollution. It was argued that poor control would reveal itself in the form of poor repeatability from one test to another. A completely automated system consisting of three controlling mechanisms and three sensors was used to precisely control the flow, temperature, and the relative humidity of the inlet air. This HCS-301 Miller-Nelson Environmental controller is equipped with panel lights on the control module that indicate if appropriate water pressure, water level, and air flow are available. After being dehumidified, and purified (*by using Dehumidifier and the Catalytic Oxidizer*), the air enters the control module through the air-flow controller that maintains and displays the flow at standard conditions (23 °C, 1 atm.) regardless of temperature and pressure variations in the flow system. From the air-flow controller the air passes through a humidification system consisting of a reservoir in which water is maintained at a constant level and a heater that produces the desired humidity, which is set using the humidity-control potentiometer. The heater runs continuously if the humidity is below the setpoint, operating intermittently as the setpoint is approached. Just before the humidified air leaves the control module, it is heated to the desired temperature, which is set using the temperature-control potentiometer. Sensors located in the corner of the test chamber measure temperature and humidity, which are read on the temperature and humidity panel meters. Appendix A.4 gives complete detail about the procedure to calibrate the temperature and humidity sensor.

Figure A.5 Air Flow Environmental Controller

A.2 FULL SCALE TEST CHAMBER

A.2.1 Overall Full Scale Chamber Description

As stated earlier, verification of scale-up requires data from either real buildings or large test chambers. Without this step, the usefulness of a model cannot be justified. However, when performing scale-up verification, data from large test chambers are preferred to those from complete buildings because the conditions in a building are difficult to control. The most important uncontrolled factors include varying air exchange rate, multiple air zones, and strong adsorption on many different surface materials (*sink effect*).

Therefore, a large chamber, sized ($55m^3$) is used for model validation purposes. The chamber has inner dimensions of ($5 \times 4 \times 2.75 \text{ m}$), with all the interior surfaces of the chamber made of stainless steel sheets. The full-scale chamber consists of:

- (i) independent HVAC (*Heating, Ventilating and air-conditioning*) unit.
- (ii) the (55 m^3) stainless steel room
- (iii) an air sampling analysis unit
- (iv) the data acquisition unit

All the aforementioned units are located in an air-conditioned laboratory space with temperature $23^\circ\text{C} \pm 1$, and relative humidity $50\% \pm 5\%$. Before presenting more details about the main test chamber units, it is worth mentioning here that a series of tests have been conducted by the materials emission project team (Zhang, et al. 1996) to evaluate the performance of the full scale chamber. Results indicate that the test facility could provide accurate control of the environmental parameters including temperature, airflow rate, relative humidity, and the chamber pressure. The table below (Table A.1) summarizes the IRC full-scale chamber operating conditions and the accuracy of control of each parameter.

Table A.1 IRC full-scale chamber operating parameters

	Temperature, $^\circ\text{C}$	Relative Humidity %	Airflow Rate, l/sec
<i>100 % Exhaust</i>	15-35	20-80	2.5-142
<i>100 % Recalculation</i>	15-35	20-80	2.5-142
<i>Control accuracy on the return air</i>	± 0.5	± 5	$\pm 3.0 \%$ or $\pm 0.3 \text{ l/s}$
<i>Control accuracy on the exhaust air</i>	N/A	N/A	$\pm 3.0 \%$ or $\pm 0.3 \text{ l/s}$

Figure A.6 Photograph of the Full-scale chamber test facility

A.2.2 Test Chamber Envelope

The chamber has inner dimensions of $5 \times 4 \times 2.75 \text{ m}$, and in order to minimize any possible sink effect, all the interior surfaces of the chamber are made of stainless steel sheets. The ceiling and the walls consist of three main layers of: (i) stainless steel sheets of type 304, No. 4 (11 gage sheets for the floor and 14 gage sheets for the ceiling and walls), (ii) 0.5" plywood, and (iii) a 4" thick fiber glass insulation layer. The test chamber is equipped with a (4.75 ft by 6.33 ft) door, and the door has an (18 in by 18 in) observation window in it. Teflon gaskets were used for sealing the door, light fixture, window, and the electrical outlet.

A.2.3 The HVAC Unit

In this unit the outdoor air is first preheated in the air preconditioning unit by means of an 8- Kw, 3 stage electrical heater. Then the air is dehumidified by passing through a chilled water coil. A single speed air fan is used to circulate the air in the preconditioning loop. In order to remove any organic compound in the air, the preconditioned air is passed through an activated carbon adsorber contained in a stainless steel box. In order to precisely control the temperature and relative humidity, the preconditioned air is passed through another two chilled water cooling coils, hot water reheat coil, and the steam humidifier. Up to this stage the chamber supply air is free from any possible outdoor contaminants, and both temperature, and relative humidity are adjusted to the desired values.

After controlling the quality of the chamber supply air (*temperature, relative humidity, and the contamination level*), the quantity of the supply air (*air flow rate*) is controlled by means of orifice plates at the outdoor supply air, preconditioning loop, immediately before the activated carbon adsorber box, immediately before and after the chamber, and finally at the exhaust duct. A stand-alone controller (*direct digital control*) controls the operation of the system, and displays and records the operation conditions on a microcomputer. Since the airflow patterns of the inlet air will be affected by the diffuser air jet, the test chamber can be equipped with four types of air outlet diffusers. These diffusers will simulate the various air flow patterns, velocity level, and the air mixing characteristics encountered in real indoor spaces.

Figure A.7 Four types of air distribution outlets in the test chamber

It should be pointed out that in order to check the cleanness of the HVAC unit, the test chamber was designed so that samples from different locations (*before and after the HVAC unit*) can be extracted.

A.2.4 Air Sampling Analysis Unit

As in the small test chamber, there are two ways to collect and analyze the air samples. The first method is known as the *direct sampling and analysis method*, and the second one is known as the *tube sampling and GC/FID analysis method*. In the direct sampling method the hydrocarbon analyzer equipped with a flame ionization detector is used. The

air samples are pumped through the total hydrocarbon analyzer pre-calibrated by using standard Cyclohexane (C_6H_{12}). This method is recommended when only TVOC needs to be monitored continuously.

The tube sampling and GC/FID method is used when both TVOC (*total volatile organic compounds*) and individual contaminants need to be quantified. From any sampling location the air sample is pumped through the commercially available sorption tube for collection of the VOC. After pumping the proper volume through the sorption tube, the collected contaminants are then thermally desorbed into a helium stream and automatically injected into Varian's Star 3400CX gas Chromatograph (GC) column which had a starting temperature of 50 °C and stayed at this point for 12 min before it was raised to 120 °C in steps of 10 °C per minute.

A.2.5 The Data Acquisition Unit

The main components of the data acquisition unit are *(i)* the interface boards for measuring the temperature, relative humidity, pressure, velocity, concentration, and the air flow rate, and *(ii)* micro-computer equipped with commercially available software for processing and displaying the data. All sensors must be calibrated before starting the test.

A.3 REVIEW OF THE DIFFUSION MEASUREMENT METHODS

Table A.2 Characteristics of the best methods of measuring diffusion coefficients

	Nature of Diffusion	Apparatus Expense	Apparatus Construction	Concentration Difference req	Method Of Obtaining Data	Overall Value
The Four Best Methods						
<i>Diaphragm Cell</i>	Pseudo-Steady State	Small	Easy	Large	Conc at known time, req chemical analysis	Excellent simple equipment
<i>Infinite Couple</i>	Unsteady in an infinite slab	Small	Easy	Large	Conc vs position at known time	Excellent restricted to solid
<i>Taylor Dispersion</i>	Decay of a pulse	Moderate	Easy	Average	Refractive index vs time	Excellent, especially for dilute solutions
<i>Capillary Method</i>	Unsteady out of finite cell	Small	Easy	Average	Conc vs time requires radioactive counter	Good but used only with radioactive tracers
Three Very accurate Methods						
<i>Gouy Interferometer</i>	Unsteady in an infinite cell	Large	Moderate	Small	Refractive grad vs position and time	Good
<i>Rayleigh or Mach-Zehnder</i>	Unsteady in an infinite cell	Large	Difficult	Small	Refractive index vs position and time	Good, best for conc Dependent diffusion
<i>Bryngdahl</i>	Unsteady in an infinite cell	Large	Difficult	Very Small	Refractive index vs time	Very hard to use, but suitable for very dilute solutions
Other Interesting Methods						
<i>Laser Doppler light scattering</i>	Homogeneous solution	Large	Difficult	None	Scattered light measurements with photo tube	Good, results sometimes hard to interpret
<i>Spinning Disc</i>	Dissolution of solid or liquid	Small	Easy	Large	Conc vs time	Good required diffusion controlled dissolution
<i>Wedge Interferometer</i>	Unsteady in an infinite cell	Moderate	Easy	Large	Refractive index vs time	Fair, much harder to use
<i>Steady state Methods</i>	Steady diffusion across known length	Moderate	Moderate	Large	Small conc changes required exceptional analysis	Fair, very difficult procedure
<i>Loschmidt method</i>	Unsteady in a finite cell	Moderate	Moderate	Large	Conc at known time	Fair
<i>Harned conductance method</i>	Unsteady in a finite cell	Moderate	Easy	Average	Electrical resistance vs time	Poor, restricted to electrolytes, and hard to use

A.4 DETAILED DESIGN OF THE SPECIMEN HOLDER

Figure A 8 Detailed Design of the Specimen Holder

Figure A 8 Continued

Figure A 8 Continued

A.5 DETAILED DESIGN VIEWS OF THE DIFFUSIOMETRIC APPARATUS

Figure A 9 Detailed Design of the Diffusiometric Apparatus

Figure A 9 Continued

Figure A 9 Continued

APPENDIX -B

CALIBRATION AND ROUTINE EXPERIMENTAL PROCEDURES

B.1 SYRINGE SAMPLING PROCEDURE

The syringes sampling procedure was conducted according to the following steps.

- (1) The compressed air supply (*carrier gas*) was Adjusted to approximately 250 (*ml/min*).
- (2) The suction pump flow rate was adjusted to approximately 150 (*ml/min*).
- (3) The thermal adsorbent tube was inserted between the injection septum and the suction pump (*see Fig. B.1*).
- (4) The designed volume was extracted from the glass vial by using air tightness syringes.
- (5) The excess air valve was opened
- (6) The needle was inserted into septum and the air sample was slowly expelled to ensure that the suction flow is greater than the syringe expulsion rate.
- (7) The carrier gas flow was turned off, and the suction line was removed from the tube.
- (8) The desorption tube was removed and analyzed by gas chromatography (*GC/FID*).
(*make sure that, your tubes are clearly labeled for future reference*).

Figure B.1 Syringe Sampling Set-up

B.2 GC/FID CALIBRATION

Standard cylinders with known concentrations are used for the *GC/FID* calibrations. Syringe samples of the gas mixture are adsorbed onto thermal desorption tubes. The samples are then desorbed onto the *GC/FID* for analysis and calibration. The calibration curves were obtained by fitting the peak area outputs to the compound concentrations. A

typical calibration procedure for the *GC/FID* is summarized in the following steps (*Refer to Figures B.2 and B.3 below*);

- (1) Fully open the valve on Rotameter A
- (2) Open valves V1 and V2 on the ultra zero compressed air cylinders. And adjust the pressure regulator to 12 PSIG.
- (3) Allow the airlines to flush for 2-3 minutes.
- (4) Put the clean sampling tube as shown in the figure (*Note the suction pump and the mass flow controller are closed*)
- (5) Set valve switch to "control" position and turn the pump on (*Note the ball in the Rotameter A should be floating at 0.07 SCFH*).
- (6) Replace the septum in sampling Tee if necessary
- (7) Select 2.5 ml gas tight syringe and check its performance.
- (8) Check the reading in both Rotameter A and Rotameter B and slowly fill/empty the sampling syringe for three times.
- (9) Collect the desired sample volume and slowly inject the calibration gas sample into the sampling tube.
- (10) Wait one minute and remove the needle from the septum.
- (11) Turn pump off, set flow controller to closed position, wait until display reads 0 then remove sampling tube and seal.
- (12) After 5 minutes turn off gases (V1 and V2) and turn the fume hood off

Figure B.2 BTX tube loading procedure

Figure B.3 BTX tube injection procedure

B.3 PROCEDURE FOR RUNNING A SET OF TUBES ON GC/FID

To run a set of samples on GC/FID, do the following steps;

- (1) Check all the GC gases and adjust the pressure regulators of the Air, Hydrogen, and Nitrogen to 60, 40 and 80 PSIG respectively.

- (2) Ignite the flame detector, by pressing the ignition button on front of the GC and leave depressed until "pop" is heard.
- (3) Reset the detector temperature by pressing <Build/Modify>, <Method>, <Detector>, and 300 °C then press <Enter>.
- (4) Allow the GC to warm up for of 2 hours.
- (5) Build the sample list as follows

From system control window select <File>, <Sample List>, <Open>, <OK>

Fill in the sample name and the sample ID number

Choose the location for data file (your sub-directory)

Save the sample list file and write the operator name and <OK>
- (6) Load the tubes in the desorber, and set the last sample and the position of the first tubes.
- (7) Activate QuickStart by selecting

<Screen>, <Sample List>

Enter the name of the sample list file

Enter the name of the Method used

Press <Start> to begin
- (8) When the samples are done, modify the detector temperature to 150 °C following the same procedure described in step 3
- (9) Turn off the Air, N₂ and H₂ gases at the GC knobs and the Air and the H₂ at the tanks.

B.4 PROCEDURE FOR CLEANING A SET OF THERMAL DESORPTION TUBES

After being analyzed in the *GC/FID* the thermal desorption tubes must be cleaned by using the Envirochem Multi-Tube Conditioner (*See Figure B.4*). The cleaning procedure is performed according to the following step:

- (1) Turn on the Helium valve behind the conditioner unit
- (2) Put the tubes to be cleaned in the holder
- (3) Turn on the main power on
- (4) Turn on individual Helium valves on
- (5) Check the Helium flow rate by using the ADM3000 flow meter.
- (6) Adjust the Helium flow rate if necessary to 60 (Cm^3/min)
- (7) After 20 minutes place the heat jackets over the tubes.
- (8) Turn on individual power supply for each tube
- (9) After 20 minutes turn off the individual power supply and leave the heating jackets on
- (10) After 20-30 minutes the temperatures will return to initial temperature, remove the heating jackets and turn the main power supply off.
- (11) Remove the clean tubes and place them in individual sleeves

Figure B.4 Envirochem Multi-Tube Conditioner

B.5 GAS CHROMATOGRAPHY

After the air sample was taken the tubes were closed tightly and analyzed as soon as possible on the gas chromatograph. As shown in Figure B.5, the gas samples were put in one of the Multi-tube Desorber, Envirochem, model 8916. After the air samples was removed from the tube by thermal desorption, the gas was then concentrated using Envirochem's Unacon 810X. The concentrated air stream is then automatically injected into Varian's Star 3400CX gas Chromatograph (GC) column.

In order to achieve good peak separation, the method for best peak separation was established. By running headspace samples of the test materials in seven different temperature programs on *GC/FID* column, the best method was selected for each product. For example in the particleboard case, the WOOD1.mth designated method was used with temperature program including an initial column temperature of 50 °C hold for 12 minutes, then heated to 110 °C at a rate of 2 °C per minute, then to 240 °C at a rate of 15 °C per minute and held for 5 minutes. More details about the separation methods and the *GC/FID* calibration is given in Appendix A-2. The column was a capillary column of the type DB-5 (60 m long, 0.32 mm ID, 0.25 µm film thickness). Helium was used as the carrier gas. The process of gas chromatography and identification of VOC's with flame Ionization Detector (*FID*) was controlled by computer software. It should be pointed out that, the *GC/FID* gives the results in the form of characteristic peaks at different retention times. These peaks are then compared with the *GC/MS* results to determine which peaks from the *GC/FID* spectrum correspond to the *GC/MS* peaks. In general the heavy compounds (*compounds with high molecular weights and high boiling points*) will show-up later on the GC spectrum.

Figure B.5 Multi-tube Desorber Unit

B.6 HOT-WIRE ANEMOMETER CALIBRATION PROCEDURE

The calibration procedure of the hot-wire anemometer consisting of two parts. The first part is the IFA-100 Flow Analyzer Calibration and the second part is the TSI Wind Tunnel Calibration.

B.6.1 IFA-100 Flow Analyzer Calibration

- (1) Turn on the power of the manometer and the IFA 100 Flow Analyzer. After about 30 minutes record the initial offset reading of the manometer.
- (2) Select channel #3 on the channel panel
- (3) Then determine the magnitudes of the cable resistance, and the hot wire probe resistance. The cable resistance can be measured by putting the null resistance probe

in the socket of the probe holder and pressing the **RES MEAS** and **LED** to display the **OPERATE RES CONTROL**.

- (4) Adjust the **OPERATE RES CONTROL** reading to zero value.
- (5) Press **RES MEAS** and **LED** again the probe cable resistance will display. Record the cable resistance by pressing **ENTER**.
- (6) The hot wire probe resistance was measured by putting the hot wire probe in the socket and the steps 4 and 5 were repeated.

B.6.2 TSI Wind Tunnel Calibration

- (1) Unscrew the two thumbscrews at the rear of the test section and remove the rear test section cover.
- (2) Slide the required orifice plate into the test section. In our case nozzle plate No. 1 was used (*since the velocity range in the chamber is relatively low*).
- (3) Make a copy of the data sheet, which is provided with the tunnel. And fill in the model number and the serial number of the velocity transducer.
- (4) Record the pressure and temperature of the test room and calculate the air density correction factor (**K**) using the equation given by the manufacturer.
- (5) Loosen the probe compression fitting and insert the hot-wire into the test section.
- (6) Align the hot-wire with the flow direction. And switch on the motor speed controller and turn the control knob clockwise until the motor starts.
- (7) Slowly increase the motor speed until the required pressure reading is reached.
- (8) Start the data collecting software ROOMAIR. And record the corresponding voltage reading.

- (9) Repeat the procedure until the calibration is finished. Table B.1 gives a sample of the calibration data sheet.
- (10) Process the calibration data and determine the calibration equation. The figure (Figure B.6) below illustrates the hot wire anemometer calibration curve.

Table B.1 Hot Wire Calibration Data Sheet

Hot-Wire Model 31-31			
<i>Room Temperature 21.5 °C</i>			
<i>Barometric Pressure 761.35 (mm-Hg)</i>			
<i>Density Correction Factor (K) 0.99868</i>			
<i>Plate # 2 (0.25" holes)</i>			
<i>Standard Velocity (m/sec)</i>	<i>Standard Pressure P (mm-Hg)</i>	<i>Desired P (P x K) (mm-Hg)</i>	<i>Velocity output (Volt)</i>
0.75	2.94	2.942	0.7265
0.6	1.87	1.877	0.7206
0.5	1.28	1.300	0.7176
0.40	0.799	0.800	0.7014
0.30	0.440	0.450	0.6841
0.25	0.302	0.305	0.6718
0.2	0.193	0.194	0.6600
0.15	0.108	0.109	0.6463
0.10	0.048	0.049	0.6300
0.05	0.012	0.013	0.6046
0.025	0.003	0.003	0.5869
0	0	0.000	0.5621

Figure B.6 Hot Wire Anemometer Calibration Curve

B.7 TEMPERATURE AND HUMIDITY CALIBRATIONS

The temperature and humidity in the test chamber were calibrated using the Vaisala Chilled Mirror probe. The reading of the room sensor and the corresponding voltage outputs were recorded along with the Chilled Mirror values. The following procedure was used for calibrating the chamber temperature sensor;

- (1) Start the VIEWDAC software and activate the data acquisition system
- (2) Turn on the Meloy environmental controller
- (3) Allow the equipment to warm up for about 30-40 minutes. Then, select channel 1 of VIEWDAC and reset the calibration equation to $x=y$.
- (4) Then reset the calibration equation in channel 2 to $x=y$.
- (5) Put the Vaisala Chilled Mirror probe near the temperature and humidity sensor of the test chamber

- (6) Select a set of calibration temperature reading. Record the blue box temperature reading and the corresponding Chilled Mirror probe reading and the VIEWDAC voltage output on channel 1 for every temperature setting.
 - (7) Obtain the best fit curve between the VIEWDAC voltage output and the temperature. This equation was input into VIEWDAC software to provide actual temperature from the environmental controller.
- The same procedure was used for humidity calibration. The only difference is that the calibration equation must be input into channel 2 instead of channel 1 in the VIEWDAC software. It should be pointed out that the above calibration procedure was repeated at the beginning of each test plan.

B.8 AIR FLOW RATE CALIBRATION

A Humonics Flowmeter with a range of 0.5-10 LPM was used to calibrate the flow into the small chamber. The calibration process was performed according to the following sequences:

- (1) Start the VIEWDAC software and activate the data acquisition system
- (2) Turn on the Meloy environmental controller
- (3) Allow the equipment to warm up for about 30-40 minutes. Then, select channel 3 of VIEWDAC and reset the calibration equation to $x=y$.
- (4) Connect the small chamber air supply to the Humonics Flowmeter.
- (5) Adjust the controller Meloy environmental to select a set of flow rate calibration range. Record the VIEWDAC voltage readings, the Meloy environmental reading and the corresponding Humonics flowmeter reading.

- (6) Obtain the best fit curve between the VIEWDAC voltage output and the Humonics flowmeter reading. This equation was input into VIEWDAC software to provide actual flow rate from the environmental controller.

APPENDIX-C

ROUTINE MATHEMATICAL AND NUMERICAL SOLUTIONS

C.1 POSITIVE ROOTS OF THE CHARACTERISTIC EQUATION

This section is devoted to illustrate the techniques and, the computer program used for finding the first positive root of the characteristic equation $\tan(q) = 2\alpha q/(q^2 - \alpha^2)$. We want to write a FORTRAN program that will search over a range of “ q ” using the increment-search method until an interval is found that contains a possible root, then switching to the bisection method for fairly rapid convergence to the root value. The flow-chart for the combined incremental-search method, and the Bisection method is shown in Figure C.1. A thorough study of the flow-chart will help in understanding how the successive Bisections are carried out, with the root always being in the subinterval to be bisected next.

The flow-chart is implemented by a subroutine subprogram called BISECT, which is called by the main program. The search increment Δq , the minimum and maximum x values defining the search region, a large value used to compare the function value to see whether it is approaching infinity, and the number of bisections to be made once a root is

bracketed by the two “ q ” values spaced a distance Δq apart are entered in the main program. They are passed to the subroutine by means of its arguments. The subroutine prints out the values of the roots determined and also sends these root values, and number of roots found back to the main program, where they can be used for further calculations.

The function for which roots are to be found $\{\tan(q)=2\alpha q/(q^2-\alpha^2)\}$ is defined in a function subprogram, which computes function values. The variable names and the quantities they represent in the program are given in the table C.1 below;

Table C.1 The Variable Name in the BISECT program.

<i>Variable Name</i>	<i>Quantity</i>	<i>Values Used</i>
X	q_i	Initial values 0.0001
XMIN	$q_{\min}$	0.0001
XMAX	$q_{\max}$	1.0
DELTX	Δq	0.000001
FMAX	$f_{\max}$	10,000
N	n (number of bisection)	30
FX	$f(q_i)$	
X1	q_{i+1}	
XAVG	$0.5(q_i + q_{i+1})$	
FAVG	$f(q_{i+1}/2)$

Figure C.1 Flowchart for subroutine subprogram BISECT

C.1.1 Program List

Main Program

```

C  BISECT.FOR
C  MAIN PROGRAM FOR CALLING SUBROUTINE BISECT
C  DEVICE * IN READ AND WRITE STATEMENTS IS THE CONSOLE
C  DEVICE 2 IN WRITE STATEMENTS IS THE PRINTER
C  * IN THE PLACE OF A FORMAT STATEMENT NUMBER MEANS FREE FORMAT
EXTERNAL F
DIMENSION ROOT(1000)
OPEN(2,FILE='2-CHA.DAT')
WRITE(*,2)
2  FORMAT('ENTER VALUES FOR XMIN,XMAX,DELTX,FMAX,N,'
* '(FREE FORMAT)')
READ(*,*)XMIN,XMAX,DELTX,FMAX,N
WRITE(2,3)XMIN,XMAX
3  FORMAT('5X,SEARCH INTERVAL IS FROM X =,F5.2, TO X =,F5.2)
WRITE(2,4)DELTX
4  FORMAT(/,6X,'WITH DELTX =,F7.3,')
CALL BISECT(F,XMIN,XMAX,DELTX,FMAX,N,ROOT,NR)
DO 5 I = 1,NR
WRITE(2,6)ROOT(I)
5  CONTINUE
6  FORMAT('5X,X =,E14.6, IS A REAL ROOT RETURNED TO MAIN')
END

FUNCTION F(X)
ALPHA=0.494848
C  ALPHA=1.3006193E-4
F=TAN(X)-(2.0*ALPHA*X)/(X*X-ALPHA*ALPHA)
RETURN
END

```

SUBROUTINE BISECT(FUNC,XMIN,XMAX,DELTX,FMAX,N,ROOT,NR)

C THIS SUBROUTINE FINDS TWO X VALUES WHICH BRACKET A REAL ROOT OF A

C FUNCTION USING AN INCREMENTAL SEARCH AND THEN CONVERGES TO THE ROOT
 C USING THE BISECTION METHOD. THE SEARCH FOR ROOTS THEN CONTINUES
 C UNTIL XMAX IS REACHED.
 C THE DUMMY ARGUMENTS OF SUBROUTINE BISECT ARE:
 C FUNC: THE FUNCTION FOR WHICH ROOTS ARE TO BE FOUND. THE CORRESP-
 C ONDING REAL ARGUMENT IN THE CALLING PROGRAM MUST BE LISTED
 C IN AN EXTERNAL STATEMENT.
 C XMIN: MINIMUM X VALUE OF REGION TO BE SEARCHED FOR ROOTS.
 C XMAX: MAXIMUM X VALUE OF REGION TO BE SEARCHED FOR ROOTS.
 C DELTX: SEARCH INCREMENT USED IN BRACKETING A ROOT.
 C FMAX: A LARGE VALUE USED TO TEST WHETHER FUNC(X) IS APPROACHING
 C INFINITY NEAR A DISCONTINUITY OF THE FUNCTION.
 C NR: THE NUMBER OF BISECTIONS TO BE CARRIED OUT IN CONVERGING
 C TO A ROOT.
 C ROOT: AN ARRAY STORING THE ROOT VALUES FOUND. THESE VALUES ARE
 C RETURNED TO THE MAIN PROGRAM FOR USE AS DESIRED.
 C NR: THE NUMBER OF ROOTS FOUND. THIS VALUE IS RETURNED TO MAIN.
 C DEVICE 2 IN THE WRITE STATEMENTS IS THE PRINTER.

DIMENSION ROOT(1000)

WRITE(2,1)

1 FORMAT(' 5X,ROOT DETERMINATION BY THE BISECTION METHOD')

NR = 0

X = XMIN

3 FX = FUNC(X)

4 X1 = X + DELTX

FX1 = FUNC(X1)

IF(FX*FX1)8,5,7

5 WRITE(2,6)X1

6 FORMAT(' 5X,X = 'F8.4,' IS A REAL ROOT')

NR = NR+1

ROOT(NR) = X1

X = X1 + DELTX

GO TO 3

7 IF(X1 .GE. XMAX)GO TO 16

X = X1

FX = FX1

GO TO 4

```

8  DO 11 I = 1,N
    XAVG = (X+X1)/2.
    FAVG = FUNC(XAVG)
    IF(ABS(FAVG) .GT. FMAX)GO TO 14
    IF(FX*FAVG)10,12,9
9   X = XAVG
    FX = FAVG
    GO TO 11
10  X1 = XAVG
    FX1 = FAVG
11  CONTINUE
12  WRITE(2,6)XAVG
    NR = NR + 1
    ROOT(NR) = XAVG
13  FX = FX1
    X = X1
    GO TO 4
14  WRITE(2,15)XAVG
15  FORMAT(15X,FUNCTION APPROACHING INFINITY FOR X =,F7.4,)
    GO TO 13
16  RETURN
    END

```

Some of the first positive roots of Equation (3.16) is shown in the following printout of the program BISECT.FOR .

Table C.2 First positive roots of the characteristic equation $\tan(q) = 2\alpha q/(q^2 - \alpha^2)$

α	q	α	q	α	q
0.002	0.06324	0.030	0.24434	0.142	0.52669
0.006	0.10949	0.034	0.26003	0.144	0.53030
0.010	0.14130	0.038	0.27481	0.146	0.53388
0.014	0.16714	0.042	0.28882	0.148	0.53744
0.018	0.18945	0.046	0.30216	0.2	0.62214
0.022	0.20938	0.050	0.31492	0.25	0.69273
0.026	0.22754	0.054	0.32716	0.3	0.75575

C.2 THE ADAMS-MOULTON METHODS

The general procedure used in what are now referred to as the Adams-Moulton methods was devised by an astronomer, F. R. Moulton, to integrate the differential equations of exterior ballistics and was later published in several sources (Moulton, 1976). It is a predictor-corrector method with an Adams formula usually used as the predictor equation. Because of its stability and efficiency, it is one of the more widely used methods for the numerical integration of ordinary differential equations.

From the Adams formulas for solving the first order differential equation we have:

$$y' = f(x, y) \quad (C.1)$$

Stepwise by providing a procedure for determining y_{i+1} by means of the equation

$$y_{i+1} = y_i + \int_{x_i}^{x_{i+1}} f(x, y) dx \quad (C.2)$$

The integration was carried out by approximating $f(x, y)$ with a polynomial $f(x)$ passing through points (x_i, y_i) , (x_{i-1}, y_{i-1}) , (x_{i-2}, y_{i-2}) ,, with the number of points depending on the order of the method used. The integration formulas developed were called ***open integration*** formulas because the integration had limits from x_i to x_{i+1} , which is a region extending beyond the last point for which y and y' values are known, that is, a value of y_{i+1} is determined without y'_{i+1} being known.

In the Adams-Moulton method this value of y_{i+1} determined by the Adams formula is considered to be just a ***tentative value***. Using Eq.(C.1), a ***tentative value*** of y'_{i+1} can then

be determined, and a ***closed-integration*** formula is used to determine a more accurate value of y_{i+1} (In general, closed-integration formulas give more accurate results than open formulas when the same number of known data points and same size are used.). A more accurate y'_{i+1} can then be found and, with another application of the closed-integration formulas, a still more accurate y_{i+1} as well. Iteration continues for a specified number of times or until little or no change is found in y_{i+1} .

Having discussed the main out lines of the Adams-Moulton methods, let us now represent a general Adams-Moulton corrector equation from which corrector equations of any desired order can be obtained by truncating the general equation to the proper number of terms.

The general formula is [Hornbeck, W. 1975]

$$y_{i+1} = y_i + h(f_{i+1} - \frac{1}{2}\nabla f_{i+1} - \frac{1}{12}\nabla^2 f_{i+1} - \frac{1}{24}\nabla^3 f_{i+1} - \frac{19}{720}\nabla^4 f_{i+1} - \frac{27}{1440}\nabla^5 f_{i+1} - \frac{863}{60480}\nabla^6 f_{i+1} - \dots) \quad (C.3)$$

In this study a fifth order Adams-Moulton method was used. Therefore, by truncating Eq. (C.3) to the fifth terms following y_i , yielding:

$$y_{i+1} = y_i + h(f_{i+1} - \frac{1}{2}\nabla f_{i+1} - \frac{1}{12}\nabla^2 f_{i+1} - \frac{1}{24}\nabla^3 f_{i+1} - \frac{19}{720}\nabla^4 f_{i+1}) \quad (C.4)$$

Substituting the backward difference into the above, gives the corrector-equation for fifth order.

$$y_{i+1} = y_i + \frac{h}{720} (106f_{i-2} - 264f_{i-1} + 646f_i + 251f_{i+1} - 19f_{i+3}) \quad (C.5)$$

The Adams-Moulton method is very accurate and stable for solving a set of ordinary differential equations, but it has one problem, the problem is, the Adams- Moulton methods are multiple-step and therefore, *not self-starting*. To advance the solution of a set of first-order equations from, say t_i to t_{i+1} by the fifth-order Adams-Moulton methods, requires information not only at t_i but also at t_{i-1} , t_{i-2} , t_{i-3} , and t_{i-4} .

Therefore, to overcome this problem, a self starting *fifth order Runge-Kutta* method was used to obtain the starting values as following;

$$y_{i+1} = y_i + \frac{1}{90} (7k_1 + 32k_2 + 12k_3 + 32k_4 + 7k_5) \quad (C.6)$$

Where;

$$k_1 = h f(x_i, y_i)$$

$$k_2 = h f(x_i + \frac{h}{4}, y_i + \frac{k_1}{4})$$

$$k_3 = h f(x_i + \frac{h}{4}, y_i + \frac{k_1}{8} + \frac{k_2}{8})$$

$$k_4 = h f(x_i + \frac{h}{2}, y_i - \frac{k_2}{2} + k_3)$$

$$k_5 = h f(x_i + \frac{3}{4}h, y_i + \frac{3}{16}k_1 + \frac{9}{16}k_4)$$

$$k_6 = h f(x_i + h, y_i - \frac{3}{7}k_1 + \frac{2}{7}k_2 + \frac{12}{7}k_3 + \frac{8}{7}k_5)$$

C.3 EMISSION RATE CALCULATION METHOD

Two technical terms are commonly used to describe the rate of emissions from indoor materials: emission factor (EF) and emission rate (ER or R). The major distinction between these two terms is that the former is an intensive property of the source and the latter an extensive property. In other words, for a given source, the emission factor does not depend on the size of the source, but the emission rate does ($E:R=A (E:F)$). Thus, the emission rate can be applied to both area sources and non-area sources. In this study both the emission rate (R) and emission factor (EF) are used. Once the chamber concentration data are obtained, the emission rate/factor were calculated as following:

C.3.1 Direct Calculation of Emission Factor from the Time-Concentration Profile

If there are enough chamber concentration vs. time data points, and the data are relatively smooth, a time-dependent emission factor profile can be obtained directly from the concentration data. For example, if we assume that the adsorption of pollutants on chamber walls is negligible, the mass balance for an area source in a chamber in an infinitesimal time period is:

$$V \frac{dY}{dt} = A R(t) - QY \quad (C.7)$$

where

V = chamber volume,

Y = chamber concentration

A = Area of the source,

$R(t)$ = emission rate at time t , per unit area, and

Q = inlet/outlet air flow rate.

Let $L = AV$ be the loading factor and $N = Q/V$ be the air exchange rate, we then have:

$$R(t) = \frac{1}{L} \frac{dY}{dt} + \frac{N}{L} Y \quad (\text{C.8})$$

When the concentration data have reasonable time resolution, the term dY/dt can be well represented by $\Delta Y/\Delta t$ (*The slope is approximated by the average of the slopes of the adjacent intervals*) thus:

$$\frac{\Delta Y}{\Delta t_i} = [(Y_i - Y_{i-1})/(t_i - t_{i-1}) + (Y_{i+1} - Y_i)/(t_{i+1} - t_i)]/2$$

So, if there are $n+1$ data points for concentration, $n-1$ emission factors values can be obtained by this method. However, in this study the software package *Table Curve*[®] was used to curve-fit the concentration vs. time data points. And the dy/dt term in Eq. C.8 was then calculated by differentiating $Y(t)$ with respect to time. Both equations then input into Eq. C.8 to get the emission factors for the compounds studied.

This method has broader, because it does not require that the emission rate be constant nor does it require steady state conditions. Furthermore, the emission factor calculated by this method is independent of any source emission models

C.4 DESCRIPTION OF THE COMPUTER PROGRAM

This computer model was written in FORTRAN language. In addition to the main program, it comprises five subroutines:

- (1) Subroutine START.SUB
- (2) Subroutine ADMOUL.SUB
- (3) Subroutine RKSF5.SUB
- (4) Subroutine SIMPSON.SUB
- (5) Subroutine FUNCTS.SUB

This model uses the fifth-order Adams Moulton method to advance the solution one step of any number of simultaneous first-order differential equations (Limited to 8002, however, by the DIMENSION statement in the main program). The Adams-Moulton method is multiple step and therefore, not a self-starting method (see Appendix B). To advance the solution of a set of first order equations from time " t_i " to " t_{i+1} " by the fifth-order Adams-Moulton methods requires information not only at t_i but also at t_{i-1} , t_{i-2} , t_{i-3} , and t_{i-4} . Subroutine start in file START.SUB, is called by the main program to obtain the information necessary for starting the Adams-Moulton method. The initial values of the dependent variables (concentration within the source) are sent to START.SUB from the main program via the array argument (Z). The initial value of the independent variable t (time) is also sent to the START.SUB as an argument value. Subroutine START.SUB advances the solution four steps of magnitude Δt (DELT) by calling the fifth-order Runge-Kutta subroutine in file RKSF5.SUB. The derivatives at the starting value at " t ", and at four additional points, are determined by START.SUB calling FUNCTS.SUB, the subroutine that defines all of the

first derivatives at the Z 's. These derivative values are stored by START as values at arrays $F0(I)$, $F1(I)$, $F2(I)$, $F3(I)$, and $F4(I)$. Subroutine RKSFX5.SUB is called four times by START.SUB, advancing the solution one step each time. The final $Z(I)$ values obtained are returned from START.SUB to the main program, and are the dependent variable values corresponding to the derivative values $F4(I)$. The independent variable value " t ", which is returned to the main program, also corresponds to the $F4(I)$'s (advanced four steps from the t value sent to START.SUB). The derivative arrays $F0$, $F1$, $F2$, $F3$, and $F4$, are returned to the main program via arguments of START.SUB.

After calling START.SUB, the main program has the information needed to advance the solution by the Adams-Moulton method. Subroutine ADMOUL.SUB is then called, sending values of Z , $F0$, $F1$, $F2$, $F3$, $F4$, and t to that subroutine. They return to the main program advanced by one step. After checking to see whether t has advanced to a value where a printout is required or the run is terminated, ADMOUL.SUB is again called for the next step, and the process continues until the desired range of integration has been covered. The predicted values of the Z 's, in advancing one step, are obtained using the Adams fifth-order formula. The corresponding FORTRAN statement precedes CONTINUE statement2 in ADMOUL.SUB.

Array name PZ5 is used for these quantities. The Moulton fifth-order corrector equation is used to obtain more accurate values of the dependent variables. Array name Z5 is used for these quantities. The FORTRAN corrector statement precedes CONTINUE statement 3 in ADMOUL. Note that, it is applied three times to iteratively improve the accuracy.

An error analysis is made at each step, and the error estimates are added to the Z's for improved accuracy. The error estimates of the fifth order Adam-Moulton method are given by the FORTRAN statement;

$$\text{ERR}(I) = -27.0 * (Z5(I) - \text{PZ5}(I)) / 502$$

For this operation the Z5(I)'s are the final corrected values of the dependent variables, and the PZ5(I)'s are the predicted values. The error array is returned to the main program at the end of each step. One or more of the array elements can be monitored to determine whether a step-size change is required. If a step size change is made, subroutine START can be used for restarting with the new step size.

C.5 CHEMICAL POTENTIAL PRINCIPLES

Near equilibrium, the flow is linearly proportional to the driving force, which means;

$$J_{xK} = -L_K \frac{1}{T} \left(\frac{\partial \mu_K}{\partial x} \right) \quad (\text{C.9})$$

where,

J_{xK} is the diffusion current of species "K"

L_K is the linear phenomenological coefficient

μ_K is the chemical potential of species "K"

For an ideal fluid mixture; (Van Wylen, G. and Sonntag R. 1982)

$$\mu(P, T, x_K) = \mu(P, T) + RT \ln x_K \quad (\text{C.10})$$

where,

P is the pressure

T is the temperature

x_K is the mole fraction per unit volume of species "K" which is generally a function of position

The mole fraction can be expressed as;

$$x_K = \frac{n_K}{n_{tot}} \quad (C.11)$$

where n_K is the mole number density of component "K"

If it is assumed that the change of n_{tot} is insignificant due to diffusion then, differentiating

Eq. C.11 in logarithmic form yields

$$\frac{\partial \ln x_K}{\partial x} = \frac{\partial \ln n_K}{\partial x} - \frac{\partial \ln n_{tot}}{\partial x} \quad 0$$

Substituting Eq. (C.10) into Eq. (C.9) yields;

$$J_{\nu K} = -L_K R \frac{1}{n_K} \frac{\partial n_K}{\partial x} = -D_K \frac{\partial n_K}{\partial x}$$

Equating the net flow to the rate of change of mole number, then

$$\frac{\partial n_K(x,t)}{\partial t} = -\frac{\partial J_{\nu K}}{\partial x} = D_K \frac{\partial^2 n_K(x,t)}{\partial x^2}$$

which is the transient diffusion equation of species "K" in the x direction