MEASUREMENT OF BIOGENIC HYDROCARBON EMISSIONS FROM VEGETATION IN THE LOWER FRASER VALLEY, BRITISH COLUMBIA.

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ABSTRACT

Biogenic volatile organic compounds (VOCs) are a diverse class of hydrocarbon released during the normal physiological processes of some species of vegetation. These substances can participate in many chemical reactions and in some cases have potential to promote the formation of ground level ozone. The Fraser Valley located in southwestern British Columbia occasionally experiences these air pollution episodes during the summer. In order to effectively reduce the frequency and magnitude of these episodes, it is important that we understand the relative role of biogenic hydrocarbons from the abundant vegetated surfaces in the region.

The thesis presents the results of measurements conducted on four common tree species in the lower Fraser Valley using a branch enclosure apparatus. Hydrocarbon emission rates from Cottonwoods trees were approximately one hundred times greater than those from coniferous trees and were dominated by the compound isoprene. Monoterpenoid emissions from four tree species were highly variable in magnitude and demonstrated no statistically significant relationship with temperature. Comparison of the observed results with a simple model from the literature shows relatively close agreement in the case of isoprene but poor agreement with monoterpene emissions. Results of these branch enclosure studies were extrapolated to larger scales to yield an areal emission rate assuming reasonable biomass densities. Isoprene measurements in this study reveal an areal emission rate approximately twenty times that of the assumed value in current emissions inventories. This discrepancy could be quite significant considering its magnitude and the possible sensitivity of the chemical reactions that produce ground level ozone to changes in isoprene concentration.

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1. Introduction

1.1 Background

Biogenic volatile organic compounds (VOCs) are a structurally diverse group of hydrocarbons released during the normal physiological operation of vegetation. They are considered secondary plant products since not all species emit these substances and they are not essential for the survival of an individual plant. Instead, these hydrocarbons appear to be specific adaptations that improve the evolutionary fitness of a species. Some of these substances are common to most plant emissions while others are released from a limited number of related species (Taiz and Zeiger, 1991). One of the main groups of compounds found in biogenic hydrocarbon emissions are the terpenes with the chemical formula $C_{10}H_{16}$. The basic building block of the terpenes is the compound isoprene (C_5H_8) commonly referred as a hemiterpene or half a terpene. The addition of more isoprene molecules yields larger terpenoid compounds such as sesquiterpenes (three isoprene molecules) or diterpenes (four isoprene molecules). In addition to there being terpenes of different molecular weight, there is a great variety of structure for each size of terpene (See fig 1.1). However, both isoprene and the terpenes are thought to be manufactured in the same biochemical pathway within the plant (Tingey et al., 1991, Sharkey et al., 1991)

Isoprene and terpenes are generally the dominant hydrocarbons emitted from healthy vegetation (Lamb 1987, Juuti et al., 1990, Khalil and Rasmussen, 1992) although in some plant species non-terpenoid compounds can make up a large proportion of emissions (Tingey et al., 1991). One of the roles served by the terpenes is the repelling of insect pests or grazing animals (Lerdau, 1991). Another possible role ascribed to them is that they serve as allelopathic agents, although this particular function remains somewhat controversial (Banthorpe, 1991, Tingey et al.

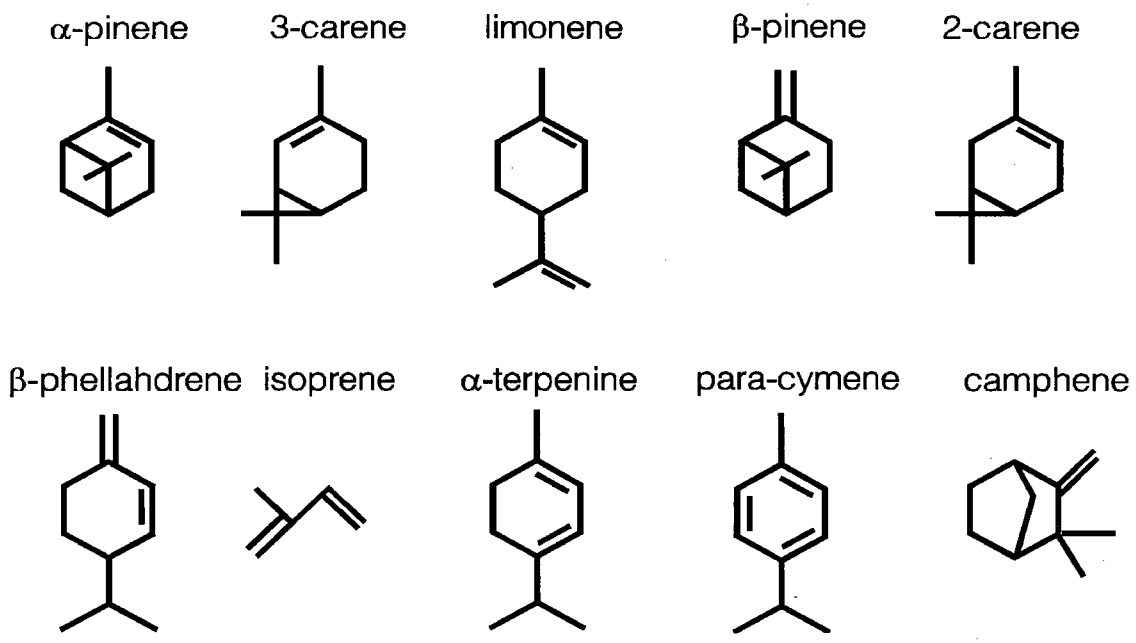

Figure 1-1: Some of the more common biogenic terpenoid compounds observed from plant emissions. Isoprene is the only substance which is not strictly a monoterpene.

1991). At present, a large number of these compounds have unknown functions yet are released at relatively high rates and present a considerable metabolic cost to the plant. In some cases, it has been found that up to 8% of the assimilated carbon during photosynthesis is released in the form of volatile hydrocarbons (Monson and Fall, 1989) but usually the upper limit of the emission rate approaches 2% (Fall, 1991, Tingey, 1981).

It is now known that biogenic hydrocarbons can participate in the formation of ground level ozone under certain conditions (Brewer, 1983, Lamb et al., 1987, Chameides et al. 1988). Although the chemistry is exceedingly complex with many different reaction pathways occurring under different environmental conditions and a whole spectrum of potential hydrocarbon precursors, the fundamental process can be summarized by equations 1.1 to 1.9 as explained by Seinfeld (1991). Equation 1.1 and 1.2 describes the photodissociation of nitrogen dioxide (NO_2), (a common pollutant emitted by combustion processes), by a photon in the wavelength range of 200 - 400 nm (represented by $h\nu$). The single excited state $O(^3P)$ atom then reacts with molecular

oxygen to form an O_3 molecule. Equation 1.3. shows that the equilibrium concentration of ozone is directly proportional to the concentration of nitrogen dioxide and inversely proportional to the concentration of nitric oxide (NO).

$$NO_2 + h\nu \leftrightarrow O(^3P) + NO \quad \text{(Rate constant } k_1\text{)} \tag{1.1}$$

$$O(^3P) + O_2 \rightarrow O_3 \quad \text{(Rate constant } k_2\text{)} \tag{1.2}$$

$$[O_3] = \frac{k_1[NO_2]}{k_2[NO]} \tag{1.3}$$

In clean unpolluted atmospheres, the natural background concentrations of nitrogen oxides yield an ozone concentration of approximately 30 ppbv (Finlayson-Pitts and Pitts 1993). As would be expected for photochemical reactions, the optimal environmental conditions for ozone production are warmer temperatures and high levels of solar radiation.

With the introduction of volatile hydrocarbons, the equilibrium achieved in equation 1.3 between photochemical reactants and products is disturbed leading to increased production of ozone. Equation 1.4 through 1.9 demonstrates this process using the chemical species RH to represent a generic hydrocarbon. The first step is the partial oxidation of the hydrocarbon by the OH radical followed by the organic radical $R^\bullet$ reacting with molecular oxygen to form an organic peroxy radical ROO (equations 1.4 and 1.5)

$$RH + OH \rightarrow R^\bullet + H_2O \tag{1.4}$$

$$R^\bullet + O_2 \rightarrow ROO \tag{1.5}$$

The organic peroxy radical can oxidize nitric oxide back to nitrogen dioxide (equation 1.6) which in turn can participate in equation 1.1 to produce more ozone.

$$ROO + NO \rightarrow NO_2 + RO^\bullet \tag{1.6}$$

The organic radical $RO^{\bullet}$ will then react with or without oxygen to form a carbonyl molecule and either a HO_2 or R', an Alkyl radical.

$$RO^{\bullet} + O_2 \rightarrow \text{carbonyl} + HO_2 \qquad (1.7)$$

$$RO^{\bullet} \rightarrow \text{carbonyl} + R' \qquad (1.8)$$

HO_2, The product of equation 1.7 can oxidize another nitric oxide molecule which can also go on to photodissociate and form more ozone.

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (1.9)$$

The overall result of reactions 1.4 to 1.9 is the partial oxidation of the hydrocarbon and the reduction of nitric oxide back to nitrogen dioxide which is then able to photodissociate again (equation 1.1) to produce more ozone. Previously it was assumed that biogenic hydrocarbons were insignificant participants in these reactions due to their low concentration in urban areas (Altshuller, 1983, Dimitriades, 1981). However, it is now evident that biogenic VOC species do react photochemically and can promote the formation of significant concentrations of ground level ozone in some areas (Cardelino and Chameides, 1990, Finlayson-Pitts and Pitts, 1993).

The relative reactivity of hydrocarbons in equations 1.3 to 1.7 will vary by approximately three orders of magnitude depending on the species being considered (Carter, 1994). Some common biogenic hydrocarbons are known to be extremely effective in promoting the oxidation of NO to NO_2 with isoprene being two thousand times more effective than methane (Carter, 1994). In areas with sufficient emissions from local vegetation, an ozone reduction strategy based on the control of anthropogenic hydrocarbon emissions will be of limited value since the biogenic hydrocarbons alone would be able to re-oxidize a large amount of NO to NO_2. Lindsay et al., (1989) concluded that anthropogenic VOC emission controls in the city of Atlanta had little effect on ozone pollution because of the large amount of biogenic emissions from the surrounding areas.

The relative role of biogenic hydrocarbon emissions compared to the total hydrocarbon composition is not the only factor when considering the photochemistry of ozone pollution in a region. The ratio of the precursors NOx (total oxides of nitrogen) to hydrocarbons will also be critically important in determining the total amount of ozone formed (OECD, 1982, Seinfeld, 1991 Finlayson-Pitts and Pitts. 1993). Figure 1.2 shows an idealized example of the relationship between the equilibrium concentration of ground level ozone and the relative concentration of photochemical precursors. This type of ozone isopleth plot is developed from laboratory observations using irradiated reaction chambers with the dashed line on the isopleth ridge representing the optimum ratio of precursors for ozone formation. At the bottom right of the graph, the atmosphere is described as NOx limited so that any reduction in hydrocarbon concentration at this point will follow parallel to the ozone isopleth line and produce little effect in

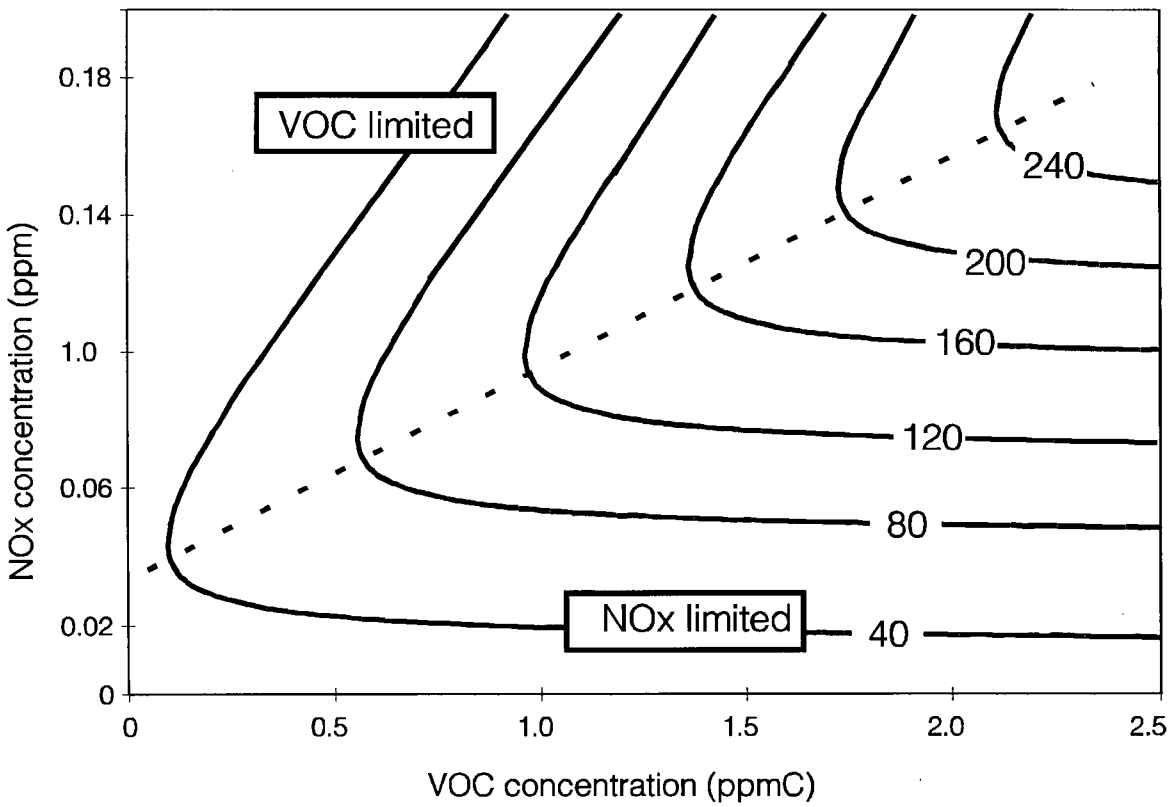

Figure 1-2: Stylized ozone isopleth plot from Finlayson Pitts et al., 1993.

reducing ozone concentration. In this case, a control strategy which limits the concentration of NOx will obviously be the most effective. Conversely the region labeled VOC limited will experience the most reduction in ozone concentration with a decrease in VOC concentration. To further complicate this problem, the relative concentrations of the ozone precursors is not static but will depend on the history of the air mass and the local sources and sinks of reactants and pollutants. It is possible however, that particular regions of an airshed can be broadly characterized by a range of [NOx] : [VOC] ratios corresponding to a certain restricted area in figure 1.2. By understanding the relative importance of the different reactants and which ones are limiting factors in the ozone forming reactions, a more effective emission control strategy can be implemented. In order to accomplish this, it is extremely important that we know the relative role of biogenic VOC in the formation of ground level ozone.

As well as being able to promote the formation of ground level ozone in certain polluted atmospheres, biogenic VOCs are important for a number of other reasons. The reactions that occur in polluted urban airsheds described in equations 1.3 to 1.7 do not cause a net consumption of the OH radical. However, in an unpolluted rural atmosphere, other chemical reaction pathways will be favored which can cause a decrease in the concentration of the OH radical. Since this chemical species is responsible for scavenging many atmospheric pollutants, any reduction in its concentration will result in a reduction of the oxidative potential of the atmosphere (Monson et al., 1991a). This could have implications for the atmospheric residence time of many radiatively important trace gases such as methane (Finlayson-Pitts and Pitts, 1993). During the oxidation of hydrocarbons in the atmosphere, it has been observed that some organic acids are formed (Lerdau 1991). Therefore emissions of biogenic hydrocarbons can also be a potentially significant source

of acid deposition in certain areas of the affecting rainwater pH and nutrient cycles (Tingey, 1991).

1.2 Review of previous biogenic VOC emission studies

Volatile hydrocarbons released from vegetation are generally classified into three broad categories which are convenient from both the standpoint of atmospheric chemistry and plant physiology. The first category consists only of the five-carbon molecule isoprene. Isoprene is unique in that it is not stored within the plant tissue but rather it is manufactured and released during the process of photosynthesis (Rasmussen, 1970, Tingey, 1981, Monson et al., 1991b). Another distinction of this compound is that it is has a much higher reactivity with the OH radical (Carter, 1991) than other biogenic hydrocarbons so that it can potentially have a disproportionately large effect on the formation of ground level ozone. The third distinction is that isoprene is emitted primarily from deciduous tree species such as oaks, maples, poplars and aspens (Lamb et al., 1987, Tanner et al., 1992). Coniferous species do emit limited amounts of isoprene but these emissions are in general orders of magnitude less than those from deciduous trees (Evans et al., 1982).

The second class of hydrocarbons is the monoterpenes, some of which give coniferous forests their distinctive smell. These compounds are synthesized and stored within plant tissue on a long term basis within leaves but can also occur in surface hairs and in some pine species within the bark (Tingey, 1991). Since these substances are present in relatively large quantities, their emission rate is generally not controlled by the rate of production in the plant but rather by the long term storage parameters and the physical characteristics of the particular compounds. In terms of chemical reactivity, the monoterpenes are approximately half as effective in photochemical ozone production when compared to isoprene. However, these compounds are released from coniferous trees in relatively large quantities so the total emission rates in areas dominated by this type of forests can be significant.

The third class of compounds are those which do not fall into the first two categories including such substances as sesqui- and di-terpenes, alcohols and other oxygenated compounds as well as other secondary plant products such as alkaloids and phenols. Their emission rates are generally much lower than isoprene or monoterpenes and their relatively low chemical reactivities dictate that they will only play a minor role in atmospheric chemistry. These compounds are also much more difficult to detect with standard equipment so they are usually neglected or ignored (e.g. Tingey et al., 1991, Altshuller, 1983). However, in some cases these substances can comprise a large proportion of hydrocarbon emissions from plant species and their importance is being re evaluated (Lamb et al., 1993, Winer et al., 1992).

Sanadze in 1957 was one of the first to investigate the subject of plant hydrocarbon emissions systematically when he discovered that certain plants emit isoprene (Sanadze, 1991). Rasmussen (1970) conducted a broad survey of 230 different plant species in a laboratory setting to determine if isoprene was released. He found that isoprene was emitted from 30% of the species examined and that these emissions occurred during photosynthesis. The emission of isoprene occurs in a diverse range of plants including ferns, gymnosperms and angiosperms yet there appears to be a large amount of variability in terms of which plants emit isoprene and the quantity released by those plants (Fall, 1991). In the early 1970's the question of whether these biogenic hydrocarbon emissions could be a factor in air pollution was examined (Rasmussen, 1972). This paper was one of the first to provide a world wide estimate of the terpene emissions into the atmosphere - between 13.5 x 10^6 t/year to 432 x 10^6 t/year compared to the estimate of 300 x 10^6 - 400 x 10^6 t/year for methane (Singh, 1992). Zimmerman (1979) conducted one of the most extensive biogenic VOC field studies done with measurements of over 600 different samples of vegetation using enclosures (described below). More recent investigations using vegetation

enclosures (for example see Khalil and Rasmussen, 1992, Lamb, 1985) have also been very useful in determining the magnitude of biogenic hydrocarbon flux from natural and agricultural surfaces.

Research into the phenomenon of biogenic VOCs began with the advent of modern analytical chemistry. However, there still remain substantial obstacles in our measurement techniques of these compounds. The complex and diverse shapes of these organic compounds dictate that their absorption spectra will also be very complicated and experience interference with more common gases such as O_2, H_2O and N_2. For this reason, attempts to measure hydrocarbon concentration using radiation absorption have met with little success. The most often used approach to measuring concentration of hydrocarbons is a gas chromatograph in conjunction with a flame ionization detector or mass spectrometer. Unfortunately these measurements are labour intensive, costly and require considerable laboratory time for the analysis of a single air sample. This lack of any fast response detector makes field measurements exceedingly difficult since real time results are not available. A chemiluminescent sensor has been developed by Hills et al., (1990) which has a response time of approximately 1 Hz at a sensitivity of 5 ppb. However, a chemiluminescent system is limited in that it can only detect one compound whereas the emissions from plant species are composed of a whole spectrum of organic molecules.

Vegetation enclosures to measure hydrocarbon flux are conceptually quite simple and do not require expensive fast response instruments. This method involves placing a bag or some other closed container around a leaf or branch of vegetation in order to capture the hydrocarbons emitted. There are two basic types of enclosure systems commonly used. A static system is one in which there is no circulation of air in the enclosure so the hydrocarbons simply accumulate within the enclosure airspace. A dynamic enclosure system has a circulating airstream which achieves a steady state of hydrocarbon production by the plant and removal by the air exchange

(See Fuentes, 1992, Lamb et al., 1985, Mosier, 1989 for examples). With both of these methods flux is calculated by measuring the change in concentration of hydrocarbons and relating this difference to the flux from the branch. Some of the practical difficulties faced with this approach include the fact that enclosing a branch can cause mechanical damage and often in full sunlight temperatures inside an enclosure can increase dramatically and expose the plant to unwanted stress. Enclosure measurements however do provide an independent check for validating other measurements techniques and can be very effective at resolving emission rates from a single vegetation species

Researchers have also used micrometeorological (Knoerr and Mowry, 1981, Lamb et al., 1985) and tracer studies (Lamb et al., 1986) to measure hydrocarbon emissions from surfaces. The lack of a fast response hydrocarbon detector has eliminated the possibility of using an eddy correlation system to measure hydrocarbon flux. Instead, the flux gradient technique has been the only micrometeorological technique available to researchers. This approach to measuring gas flux requires the ability to resolve a very small concentration difference between the two measurement heights. Unfortunately, some of the fundamental assumptions of surface layer theory required by the flux gradient approach over rough vegetated canopies are in question (Dabberdt, 1993). Recent work by Nie et al. (1995) has shown the feasibility of measuring hydrocarbon flux using a Relaxed Eddy Accumulation system which avoids many of the questionable assumptions inherent to gradient measurements and does not require a fast response detector. This method measures the difference in concentration between upwards and downwards moving eddies by sampling conditionally into two different storage reservoirs. One of the main advantages of a micrometeorological approach is that it provides an integrated view of an extensive surface's gas flux whereas enclosures only provide a hydrocarbon emission rate for a leaf or small branches.

Knowing the emission rate from a unit area is useful when trying to extrapolate to larger scales such as in the case of compiling an emission inventory over a geographical area

Lamb (1986) used a sulphur hexafluoride tracer to measure the emission rate of isoprene from an isolated stand of oak trees. In this study the tracer was released from within the stand of trees and the downwind characteristics of the plume were measured. Using the assumption that passive scalars such as isoprene and SF_6 are have similar turbulent transport characteristics, the emission rate of isoprene or any other biogenic hydrocarbon can be calculated. Simultaneous enclosure measurements showed good agreement with the tracer results. Unfortunately, site requirements for this type of study are very difficult to achieve thus severely limiting its application.

As large scale studies examining emission of hydrocarbons from branches or extensive surfaces were conducted, the biochemistry and physiology of this process was also being examined in the laboratory. There are two main laboratory techniques for investigating gas emissions from vegetation. One way of approaching the problem is to determine the response of seedlings or clipped branches to different conditions in environmentally controlled gas exchange chambers (e.g. Tingey et al., 1980, 1981, Juuti et al., 1990, Kuzma and Fall, 1993, Yokouchi and Ambe, 1984). These chambers are similar to the enclosures used in field studies but the offer the advantage of greater experimental control. The second approach in laboratory studies is to examine biogenic hydrocarbon production and emissions from the point of view of the biochemical processes (e.g. Sharkey et al., 1991 or Sanadze, 1991). Both these methods of studying trace gas emissions from vegetation have contributed greatly to our understanding about this phenomenon.

Isoprene emissions are observed to occur only in the presence of light suggesting some linkage with the process of photosynthesis. However, Figure 1.3 shows that the relationship is not a simple one since CO_2 assimilation and isoprene production behave very differently at different ambient concentrations of CO_2. Furthermore, Sharkey et al. (1991) have observed that in an atmosphere of elevated CO_2 concentrations, aspen trees increase their emission rate while the emission rate of oak trees decreases. To date there have been no satisfactory explanations

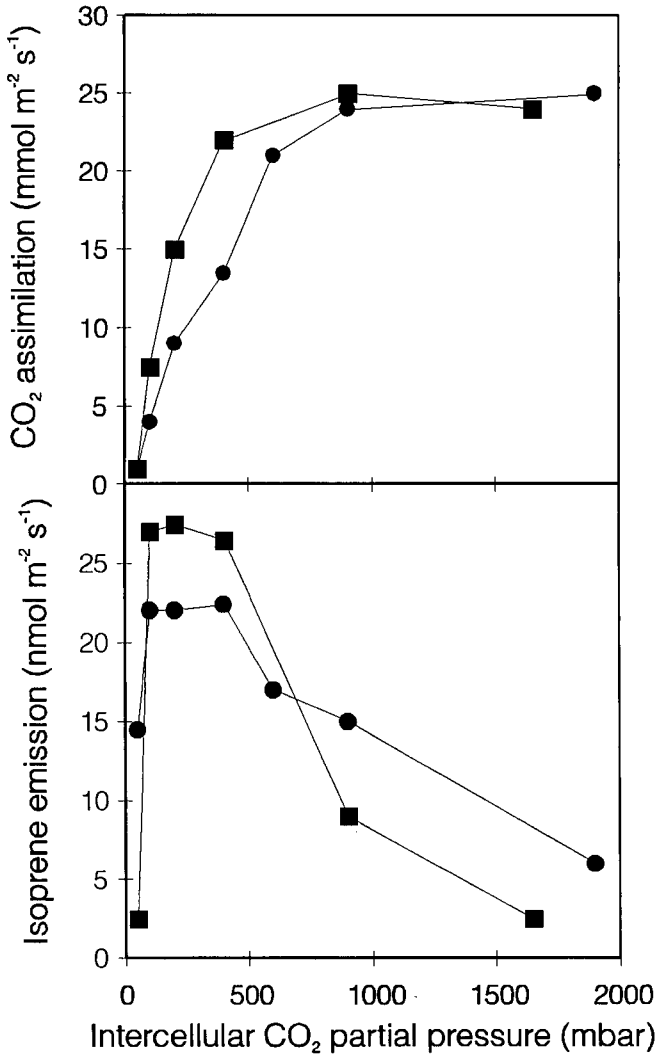

Figure 1-3: Photosynthetic carbon assimilation rate and isoprene emission rate vs. intercellular CO_2 partial pressure. Circles indicate 0 mbar O_2, squares indicate 210 mb O_2. (From Loretto and Sharkey, 1990)

regarding this behavior at different CO_2 concentrations. Studies conducted using radioactive labeled carbon dioxide($^{13}CO_2$) reveal that isoprene is manufactured almost instantly indicating that there is a close coupling between photosynthesis and isoprene production and is likely mediated through the transduction of reducing power (Monson et al., 1989). If the enzyme (Ribulose Bis Phosphate Carboxylase Oxygenase or RUBISCO) that is responsible for fixing CO_2 in the Photosynthetic Carbon Reduction (PCR) cycle is inhibited however, the rate of isoprene production remains unaffected (Sanadze, 1991). This indicates the presence of a second carbon fixation mechanism in plants and was a somewhat revolutionary discovery since previously it was assumed that all carbon fixed in the biosphere occurred via RUBISCO. Monson and Fall (1989) investigated the mechanism of isoprene production in vitro and found that under a very narrow range of pH conditions the isoprene precursors could react to form isoprene. However, they also discovered an enzyme (isoprene synthase) which converts the precursors to isoprene much faster than the non enzymatic reactions and demonstrated an optimal production rate at the pH range found in the stroma of the chloroplast.

Monson et al., (1991a) have proposed a biochemical pathway for the production of isoprene based on our current knowledge of the processes (see Figure 1.4). The first important regulatory step in this model is the carboxylation mechanism. Since it is an enzyme mediated reaction, it will occur at a faster rate at higher temperatures. The second regulatory component is the input of reducing power in the form of NADPH and ATP from the light reactions of photosynthesis to provide the energy necessary for the synthesis of isoprene. The allocation of this energy might be regulated by light modulated enzymes (Silver and Fall, 1991) but to date no exact mechanism has been proposed. This step is almost certainly that responsible for the light dependence of isoprene emissions. The third important regulatory mechanism is the activity of

the isoprene synthase enzyme. It also operates at a higher rate at warmer temperatures but at sufficiently high temperatures its effectiveness decreases because of denaturing of the proteins (Taiz and Zeiger, 1991, Guenther et al., 1991, Guenther et al., 1993). These three steps are likely the most important processes in the production and emission of isoprene and will account for the variation of isoprene emission rate with changes in photosynthetic activity and temperature.

It has been suggested that isoprene production is linked to the availability of oxygen

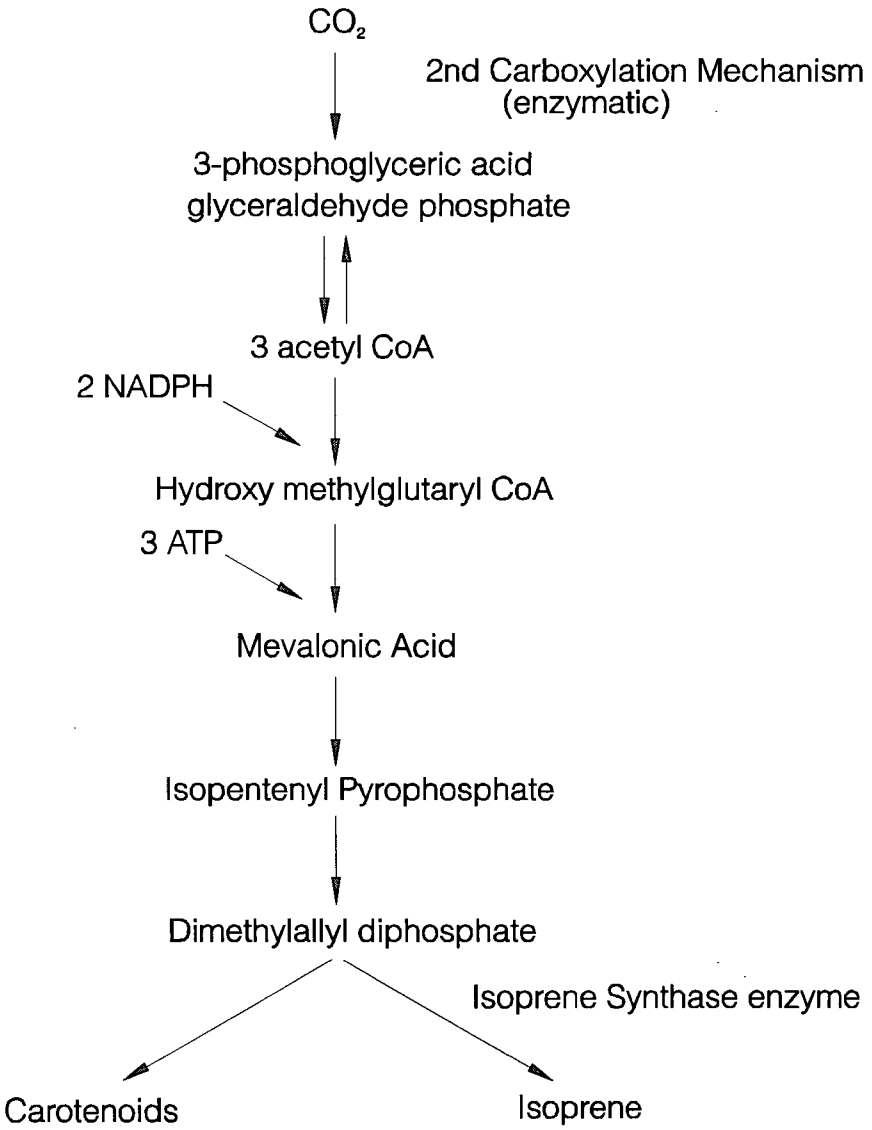

Figure 1-4 Model of the processes regulating production of isoprene. From Monson et al., (1991).

(Loomis and Croteau, 1980). This stems from the observation that plants in a CO_2 free environment are able to maintain a limited emission rate of isoprene while those in placed in an environment depleted of both oxygen and CO_2 cease all isoprene emissions. However, Monson and Fall, (1989) demonstrated that plants exposed to O_2 deficient air did not experience a substantial decrease in isoprene emission rate indicating that there is no direct link between photorespiration and isoprene emission. Further studies (Hewitt et al., 1990) using inhibitors to block the photorespiratory pathway demonstrated that isoprene emissions continue unabated. One possible explanation for the observed link between oxygen availability and isoprene emissions is that during photorespriation a small amount of glycerate is produced. This substance can then be used as a source of carbon by CO_2 starved chloroplasts allowing limited production of isoprene to briefly continue.

Recent work by Sharkey and Singsaas (1995) has demonstrated that isoprene may act as a thermal protection adaptation to prevent damage to chloroplasts at high temperatures. Thermal stress kills plants by reducing the stability of membranes eventually causing loss of cell compartamentalization and death. Experiments were conducted on plants that were not allowed to produce isoprene (by placing them in an atmosphere of N_2). Plants exposed to isoprene from an external source were able to withstand considerably higher temperatures before chloroplast damage occurred compared to plants deprived of all isoprene. This observation coupled with the observed increased allocation of carbon at high temperatures is strong evidence for the role of isoprene in protecting plants from heat damage. Plants inhabiting extremely hot areas such as deserts do not appear to emit isoprene, probably because they are exposed to severe heat stress on a long term basis and have developed more efficient thermal protection strategies (Mlot,

1995). The question of why related plants exposed to the same temperature regime show very different emission rates remains unanswered.

Emission of isoprene from a leaf appears to be almost entirely through the stomates, but the rate of emission does not appear to be controlled by the degree of stomatal closure (Tingey et al., 1981, Monson and Fall, 1989, Fall and Monson, 1992). When the isoprene flux resistance increases because of partial stomatal closure, the vapour pressure of isoprene within the stomatal cavities increases proportionately in order to compensate. Since the storage pool within the leaves is so small, the rate of isoprene emission is entirely production limited and therefore shows little relationship to the status of the stomates. For this reason, researchers have concluded that modelling of isoprene from forest canopies will be affected by stomatal closure only as it affects the energy balance (and thus temperature) of the leaf and will not have a direct influence on isoprene emission rate from a standpoint of stomatal resitance (Fall and Monson, 1992).

The second class of compounds emitted from vegetation, the monoterpenes, is a diverse group with thousands of different substances identified by the 1980's. Monoterpenes have been found in higher plants, mosses, liverworts, algae and lichens (Banthorpe, 1991). Since every different plant species has differing proportions of these hydrocarbons, emissions from a particular species will be unique, providing a possible method for identifying plants taxonomically (Lerdau, 1991). However, difficulties with collecting and identifying these compounds make this seem somewhat optimistic. As stated before, some monoterpenes are known to act as chemical defense compounds against insects and grazing animals but many of them serve no known purpose yet can represent a significant cost of resources to the plant.

Terpenes are known to be manufactured in the same biosynthetic processes as isoprene, the mevalonic biosynthetic pathway (Croteau, 1987, Tingey, 1991). In the case of monoterpenes,

two isopentenyl pyrophosphate (IPP) molecules are joined together and the pyrophosphate groups are removed to form a generic ten carbon monoterpene precursor. This initial compound then undergoes a reaction with a specific enzyme which causes conformational changes in its structure (Lerdau, 1991, Banthorpe, 1991). Types of monoterpenes produced by a plant will be controlled at a fundamental level by the genetics of the individual species which dictate the types of enzymes present to form these products. On a short term basis, the physiological health of the plant and the availability of resources will determine how efficiently these compounds are being produced. One example of an environmental control of monoterpene production is the presence or absence of nitrogen (Tuomi et al., 1988). When nitrogen is abundant, the plant will allocate more effort to the production of nitrogen containing defense compounds (alkaloids). As the availability of nitrogen decreases, the plant will switch to producing more carbon based defense compounds such as terpenes. Plants are also observed to change their terpene production according to water availability. If moisture is abundant, plant growth (by cell expansion and turgor effects) is unconstrained so more effort is allocated to synthesis of primary plant products such as starch and lignin. When the plant becomes water stressed and can no longer maintain cell expansion, the plant will switch to the production of defense compounds such as terpenes (Lerdau, 1991).

Since terpenes are stored within the leaf tissue in relatively large quantities, the rate of release of these compounds into the atmosphere will not be limited by production, but rather by the pool size within the leaf (Schindler, 1989). Temperature controls the saturation vapour pressure of these volatile compounds and so ambient temperature will be a primary factor in controlling the short term flux of terpenes from a leaf. Tingey et al., (1980) suggested that terpenes are entrained by the transpiration stream from storage locations to the stomatal cavities .

This is important since not only will the emission rate increase because of the greater vapour pressure deficit of the volatile hydrocarbon but an increase in transpiration will also allow more terpenes to escape from the plant. Evidence of this dual effect is evident in the observation that the vapour pressure of α-pinene increases at 5.6% degree^{-1} while the emission rate of α-pinene from many coniferous species is approximately 10% degree^{-1} (Tingey, 1991). Yokouchi and Ambe (1984) found that light intensity (independent of temperature) does have a small but significant effect on terpene emission while most other investigators have found no such direct relationship (Evans et al., 1985, Tingey, 1991).

Storage of monoterpenes in plant tissues causes some other uncertainties when determining emission rate from an individual plant. The pool of terpenes can be partially depleted if production rate is less than rate of losses by volatilization. In this case, the emission rate will decrease even if the optimal conditions for high emission rates are maintained (Dement et al., 1975). Another factor that leads to large increases in terpene emission rate is mechanical disturbance of a piece of vegetation. Damage will cause some of the storage areas to rupture, releasing their contents and leading to an increase in observed emission rate. This behavior is not surprising considering the fact that many terpenes are thought to be defense compounds against pest and grazing animals which cause precisely such damage to a plant. Juuti et al., (1990) found a five fold increase in terpene emission rate from a Monterey pine for up to two hours after rough handling. It is possible that even strong winds will cause mechanical stress to the plant leading to increased emission rates.

1.3 Rationale of research study

The lower Fraser Valley (LFV), located in the southwestern corner of British Columbia is a large, relatively flat area straddling the U.S.-Canadian Border. The region is surrounded by the Coast mountains on the north side and the Cascade range to the southeast while the western edge is bordered by the Straight of Georgia (see figure 1.5). During summertime, episodes of elevated ground level ozone can occur which exceed the National Ambient Air Quality Objective (NAAQO) acceptable guidelines for exposure. The synoptic and mesoscale meteorology, a very important factor in these ozone episodes, has been extensively reviewed by others (e.g. Steyn et al, 1996, Roberge, 1990) and so will be only briefly summarized here.

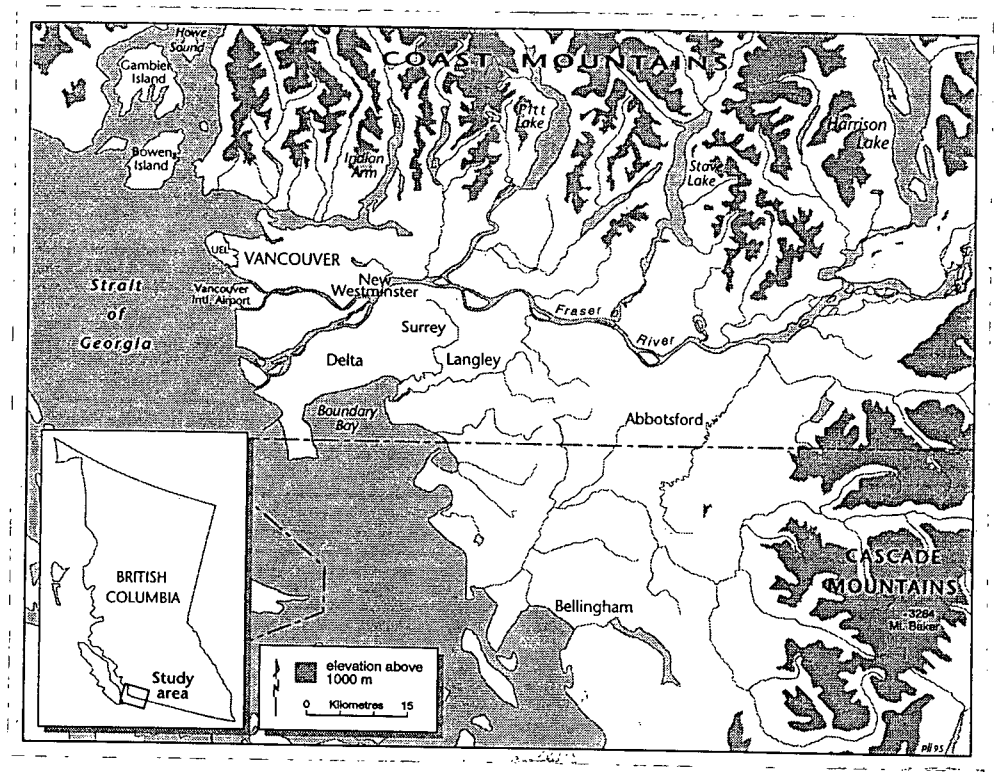

Figure 1-5: Map of the Lower Fraser Valley located in southwestern British Columbia. Urban areas are located primarily to west of Langley.

Conditions leading to an ozone episode are characterized by an upper level ridge exerting influence over the western coastline of North America. This synoptic scale ridge cause subsidence that suppresses the depth of the mixed layer height during the day. Subsidence coupled with the topographic constraints of the region and the light winds typical of a period of high pressure inhibit the horizontal advection of pollutants from the region. This stagnation of air can cause an accumulation of photochemical precursors and products leading to exceedences of the accepted air pollution standards (Pryor and Steyn, 1995). These periods of high pressure can last for many days and usually end with the intrusion of a cooler maritime air mass from the west.

Deleterious effect of ozone on both humans health and crops and forestry have been well documented (e.g. Heck, 1982, Lipmann, 1990). The NAAQO for ozone are 82 parts per billion (ppb) for 1 hour which was exceeded in the LFV on 8.5% of the July and August days between 1984 - 1992 (Pryor and Steyn, 1995). Damage to vegetation has been observed to occur at concentrations as low as 50 ppb and has been estimated to cause $9 million in lost income for agriculture in the LFV each year (Senes Consulting Limited, 1993). The photochemical reactions that produce tropospheric ozone occur on a timescale of hours so it is commonly observed that peak ozone concentration occurs downwind of the precursor sources (Steyn et al., 1996). Most anthropogenic precursor emissions in the Fraser valley originate from the densely urbanized areas in the north and western portion of the region while the rural areas in the eastern portion of the valley generally experience the highest frequency and concentration of ozone (Pryor and Steyn, 1995).

The high density of automobiles and industry in the Fraser Valley are likely the main sources of nitrogen oxides with the highest emission rates located in the most urbanized parts of Vancouver (Pryor and Steyn, 1995, Dunlop et al., 1995). The source of hydrocarbons that

participate in ozone forming reactions is much less certain. It is possible that a large amount of hydrocarbons are released from anthropogenic sources such as industry and automobiles. However, from previous measurements (Bottenheim et al., 1996) it appears that biogenic hydrocarbons that occur in the LFV could potentially be a significant ingredient for the formation of photochemical smog. The LFV region is classified as a coastal temperate rainforest and has extensive areas of natural vegetation which could be a major source of these hydrocarbons. During the warm weather associated with these ozone episodes and the increased temperatures from any urban heat island effects, greater emissions of natural biogenic hydrocarbons may play an important role in the photochemistry of ozone episodes in the region. A large area of the valley is dedicated to agricultural crops and pasture but previous investigations show that these surfaces are not a significant source of biogenic hydrocarbons (Lamb et al., 1987, Lamb et al., 1993)

Past attempts to reduce ozone concentrations in urban airsheds have concentrated primarily on reducing the emissions of anthropogenic hydrocarbons (Seinfeld, 1992) since this is much easier than controlling emission of nitrogen oxides. However, in some cases this control strategy has met with limited success because of an underestimation of the contribution of biogenic hydrocarbons, with the city of Atlanta being the most famous example (Lindsay et al., 1989). Before implementing an emissions control strategy in the Vancouver region it is therefore essential to understand the role of both anthropogenic and biogenic hydrocarbons in the formation of ground level ozone. With this information, it will be possible to implement the most cost effective control strategy to lower the frequency and intensity of ground level ozone episodes in the Lower Fraser Valley.

To investigate the emission of biogenic hydrocarbons into the LFV airshed, we must improve our understanding of the amount of these compounds released into the atmosphere. Past efforts to calculate biogenic hydrocarbon emissions from areal sources have been based on some form of equation 1.10 (Guenther et al., 1991, Lamb et al., 1993., Guenther et al., 1993)

$$E = B.R. \times T_f \times L_f \times H_f \qquad (1.10)$$

where the emission rate is the mass flux of hydrocarbon from a plan unit area per unit time (μgrams of HC meter^{-2} hour^{-1}). B.R. is the base emission rate at a particular set of environmental conditions (usually at a temperature of 30°C and a photosynthetic photon flux density of 1000 μmols m^{-2} s^{-1}). T_f, L_f and H_f are all empirically derived factors to account for changes in the base emission rate caused by changes in temperature, light intensity and humidity respectively. This equation can be coupled with canopy microclimate models and land use information to account for the horizontal and vertical heterogeneity of the base emission rates and emission factors.

Unfortunately there is a great deal of uncertainty involved in every term of equation 1.10. The base emission rate is usually obtained from plant physiology studies in the lab or from micrometeorological experiments over a vegetated surface. Lamb et al., (1987) examined the uncertainty associated with these types of emission inventories and found that most uncertainty was a result of the leaf emission rate models. Applying the emission response functions for plants exposed to environmental conditions other than those in which they were developed can also add considerable uncertainty because of genetic factors and the importance of environmental history in determining emission rates.

1.4 Research objectives

In order to compile an inventory that is as accurate as possible we must strive to reduce the amount of uncertainty within each term in equation 1.10. However, because of the huge diversity of species and the expensive nature of this type of research, a detailed study of each plant species is simply not feasible. Instead, we must determine which vegetation species are likely to be the most important emitters in order to concentrate our effort. Therefore, for this study there are three specific goals to be met which will improve our understanding of the emission of biogenic HC's. These are:

- Develop a method for measuring the emissions of biogenic hydrocarbons from vegetation in the field. This has been done in the past by numerous researchers using a variety of techniques. However, many of these approaches suffer some drawbacks. In this study a new method for field measurements of branch emission rates will be implemented which avoids most of the problems encountered in other field studies.
- Measure the emission rate of hydrocarbons from the most important contributing tree species in the LFV at different temperature and light conditions. Since the emission rate of hydrocarbons is greater at higher temperatures and light intensities, it would be useful to know the magnitude of these emissions and how they change with differing environmental conditions. This information would then be of available for those interested in modelling photochemical air pollution episodes. Choice of which tree species to examine will depend on likely emission rates and frequency of a particular species in the LFV.
- Critically evaluate the current emission inventory base rate, temperature and light factors. Currently, air pollution models simulating ozone episodes in the LFV are using an emissions inventory derived from the literature and data gathered in other geographic locations. By

using data obtained from the local vegetation, we can reduce the amount of uncertainty in the current emissions inventory for the LFV.

2. Methodology

2.1 Instrumentation

A portable dynamic gas enclosure system similar to that used by Fuentes (1992) has been constructed in order to measure flux of biogenic hydrocarbons from tree branches. This system operates on the assumption that a known volume of air enters the branch enclosure (cuvette) while the same volume of air exits the enclosure over the measurement period. Any change in hydrocarbon concentration between the two airstreams is assumed to be a result of emissions from the enclosed vegetation sample. (see equation 2.1)

$$E = \frac{F(\rho_{HC\,in} - \rho_{HC\,out})}{M} \qquad (2.1)$$

In this equation E is the emission rate of hydrocarbon released from a unit mass of branch per unit time (units of $\mu g\ g^{-1}\ h^{-1}$), ρ_{HCout} and ρ_{HCin} are the density of hydrocarbon species in the inlet and outlet airstreams ($\mu g\ m^{-3}$), M is the branch dry biomass (g) and F is the flow rate of air entering the enclosure ($m^3\ h^{-1}$).

The gas exchange system is shown in figure 2.1. Air entering the system is scrubbed of hydrocarbons by passing it through a 6-14 mesh activated charcoal filter so that ρ_{HCin} is assumed to be 0 $\mu g\ m^{-3}$. Another purpose of the charcoal is to remove any ambient oxidants which, if present, could destroy hydrocarbons and introduce unwanted measurement error. There are problems associated with the use of this type of filter such as the effective lifetime and water vapour adsorption (Mags, 1975). In order to reduce the possibility of contamination, fresh charcoal was used before each day of sampling. In spite of these precautions, some difficulties were encountered with the filter (see results section).

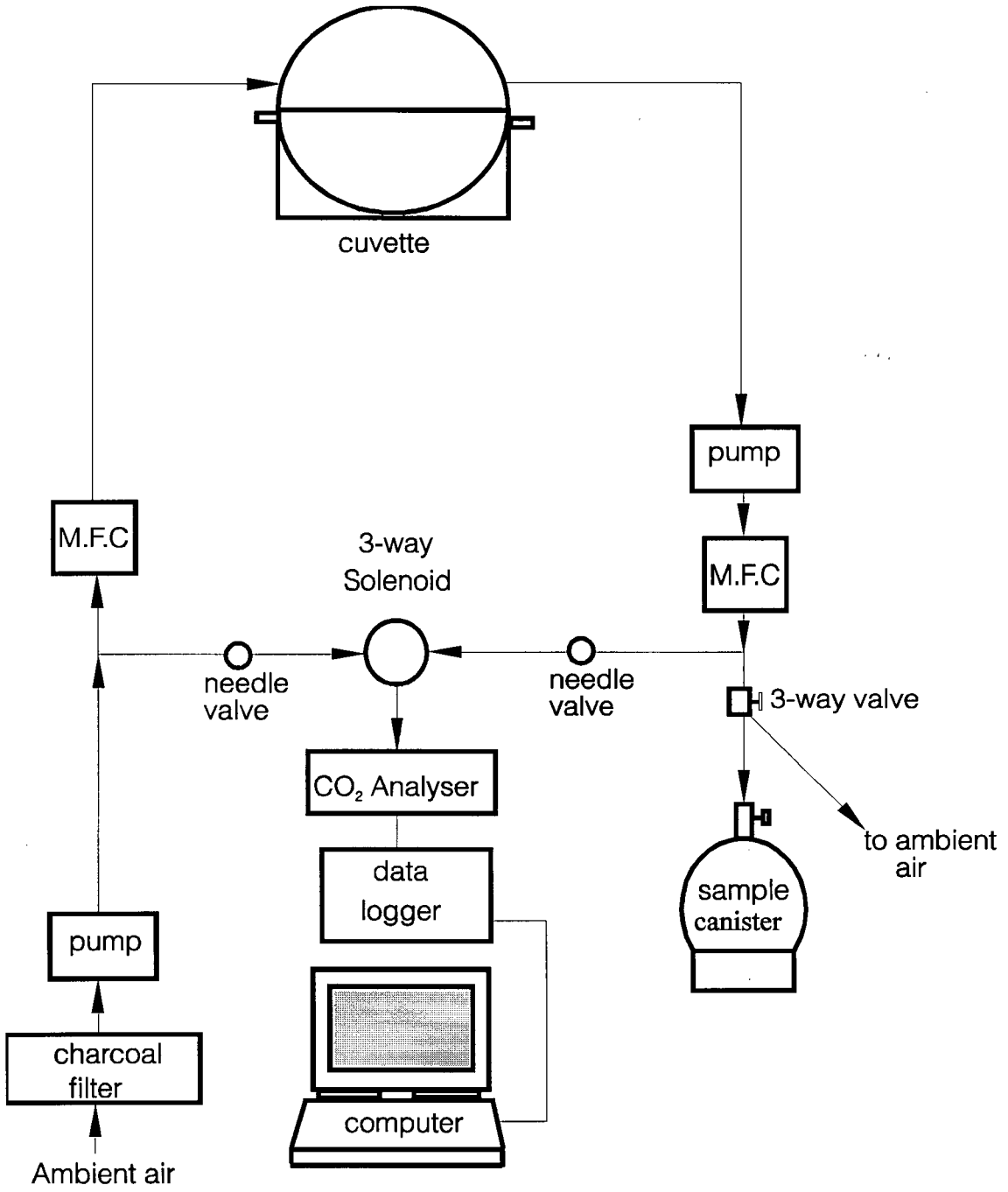

Figure 2-1: Gas exchange system used in theis study

A stainless steel 40 litre/minute metal bellows pump (model MB - 158, Metal Bellows Corp., Sharon Mass.) was used to draw air through the charcoal filter. The hydrocarbon free air was then passed through a 10 Standard Litre Per Minute (SLPM) mass flow controller (Tylan

General, Torence Ca, model FC - 261) accurate to ±1% of the full scale range. The air was then be sent to the actual branch enclosure (described below) through a 10 metre long 1/4" O.D. 1/8" I.D. Teflon lined polyethylene tube. A second stainless steel bellows pump was used to draw air through a second Teflon lined polyethylene tube from the enclosure . The flow rate of air from the branch enclosure was controlled with a 1 SLPM mass flow controller (Tylan General, Torence Ca, model FC - 260). The flow rate into the enclosure was usually 5 litres per minute while the sample line flow rate out of the enclosure was 1 litre per minute. The difference in flow rates into and out of the cuvette ensured that all leaks would be directed outwards and not draw contaminants into the system. The choice of flow rates require a compromise between efficient mixing within the cuvette and enough residency time for the accumulation of sufficient hydrocarbon concentrations to allow accurate chemical analysis. Prior to the field measurements, experiments were conducted to determine the optimal flow rates for efficient mixing (results shown in appendix 1). Air inside the enclosure was assumed to be well mixed so there is no need to sample the entire volume of air exiting the cuvette. Any fraction of the air in the cuvette should be representative of the entire volume over the time scales used in these experiments. After passing through the second mass flow controller, air collected from the cuvette was be routed through a 3-way manually controlled valve. This valve enabled sample air to be either vented to the ambient atmosphere or collected in the canisters for analysis. During field measurements the pumps were physically isolated from the rest of the equipment and sensors in order to avoid problems caused by excessive vibration.

CO_2 drawdown of the enclosed branch was measured so that rate of photosynthesis could be monitored during the experiments. This was to ensure that the plant within the enclosure was in fact photosynthesizing and not suffering any stress that would halt this physiological process.

A second reason for the CO_2 drawdown measurements was in order to observe the relative magnitudes of CO_2 assimilation rate and VOC emission. The CO_2 measurements were obtained by alternately drawing a small amount of air (approx 0.3 litres/min) at 30 second intervals from the airstreams entering and exiting the branch enclosure. Switching was done using a 3 way 120 Volt AC Teflon lined solenoid valve which then routed this airstream to the CO_2 analyzer. The CO_2 analyzer used was a Li - Cor 6262 Non dispersive Infra Red Gas Absorption (IRGA) Carbon dioxide/water vapour detector (Li - Cor corporation, Lincoln Nebraska) set to differential mode using reference air with a concentration of 365 ppm CO_2. Flow into the CO_2 detector was adjusted with two needle valves mounted before the solenoid and monitored with a 1 litre per minute flow metre located on the outlet port of the CO_2 analyzer. The tubing from the solenoid to the CO_2 analyzer had a 1/8" I.D. and a length of approximately 25 cm. This small air volume coupled with the small volume within the sample cell (approx 0.012 litres) ensured that the residency time of air between the solenoid and the detector was under three seconds and that the time constant of the CO_2 detector to the step changes in concentration would also be very small. The branch enclosure or cuvette consists of two Pyrex glass hemispheres with an internal diametre of 24 cm (see figures 2.2 and 2.3) and a total volume of approximately 5 litres. The outside edges are flanged which allowed a Plexiglas clamping system to hold the two hemispheres together during sampling. A large (4 cm square) notch is located on the upper and lower hemisphere edges to allow a branch to be placed inside the cuvette without damage.

A closed cell foam gasket wrapped in Teflon tape was placed between the two hemispheres to avoid crushing any plant parts and to seal the chamber as much as possible during sampling. The bottom hemisphere has three gas inlet/outlet 1/4" O.D. ports with standard Pyrex glass fittings and Teflon gaskets. The bottom cuvette half sits within a sealed Plexiglas reservoir

which can be filled with cold water to provide cooling when needed. A sample branch enters the cuvette through the notches and is wrapped with thin Teflon film which is held in place with alligator clips. Although this does not provide a perfect seal for the branch, it does greatly reduce the volume of air escaping from the notch while minimizing damage to the vegetation.

A Teflon encased copper constantan thermocouple was placed directly underneath the

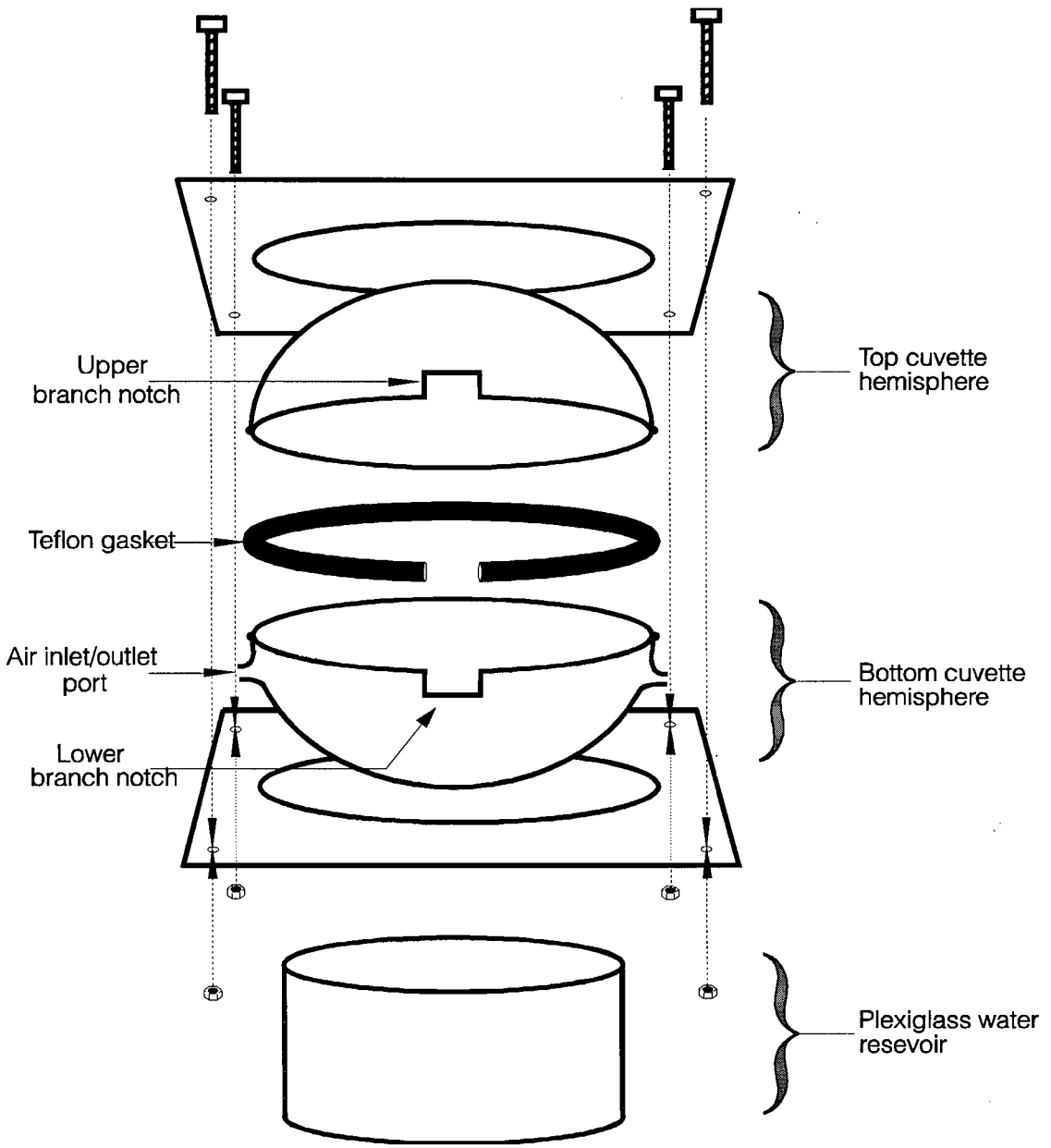

Figure 2-2: Exploded view of gas exchange cuvette

sample branch in the cuvette while another was located in a similar position on a branch outside the cuvette. These two thermocouples provided a realistic comparison of the leaf temperatures inside and outside of the cuvette while avoiding the use of adhesives to glue thermocouples to the leaves and possibly introduce contaminating hydrocarbons. When the difference in leaf temperature inside the cuvette compared to that of leaves outside achieved a certain threshold (usually 2 °C), a small bilge pump would circulate ice water from a picnic cooler into the Plexiglas container. This cooling system was relatively slow to respond because of the thermal inertia of the Pyrex glass but did allow a reasonably steady temperature to be maintained inside the cuvette during the experiments. Although the reference thermocouple within the datalogger has an accuracy of ± 0.2°C this was considered unimportant since only the difference in temperature between the inside and outside of the cuvette were being measured. As well, variability in temperature measurements caused by the positioning of the thermocouples relative to the branch were likely be considerably larger than 0.2°C.

Photosynthetically Active Radiation (PAR) was measured using a Li-Cor Li-190SA sensor (Li - Cor corporation, Lincoln Nebraska). Tests conducted outdoors under various photosynthetic photon flux densities (PPFD) indicated that attenuation through the glass lid of the cuvette was negligible (Fuentes, 1992). For this reason the sensor was placed on the outside of the cuvette directly adjacent to the upper glass dome. Temperatures and photosynthetic radiation were monitored and logged at 0.5 Hz on a Campbell Scientific 21X datalogger (Campbell Scientific Corporation, Logan Utah). This sampling frequency was chosen in order to be able to monitor short term changes in P.A.R. and temperature. Filling of the sample canister required between ten and fifteen minutes. Because the sample collection is continuous over this time period, the calculated emission rate is an average value over this time period. For this reason,

although CO_2, temperature and PAR were monitored once every two seconds, the results of these measurements were also averaged over the fifteen minute sample collection period. Experiments conducted by Hills and Zimmerman (1990) and Monson et al., (1991) have shown that hydrocarbon emissions response to changes in environmental conditions occur over a time scale of approximately ten to fifteen minutes. The datalogger also recorded the CO_2 concentrations and the outputs from the flow controllers as well as timing the alternating solenoid and providing the

Figure 2-3 Cottonwood branch inside gas exchange cuvette

analog output voltage to the flow controllers. A notebook PC computer was used to continuously monitor all of these variables enabling any problems that arose to be fixed promptly.

The rate of transpiration of the branch was not measured during these experiments since the cooling surface on the bottom of the cuvette caused considerable condensation making any accurate assessment of evaporation from the branch impossible. Condensation was not considered a problem in terms of acting as a sink for hydrocarbons because of their very low solubility in water (C.R.C., 1977).

All of the electronic instruments required either 120 Volt AC power or 12 volt DC power supplied by a portable gasoline generator used in conjunction with a 4 amp 12 volt power supply unit. The generator was placed approximately 50 metres downwind from any sampling site to ensure that fumes were not drawn into the gas exchange system. When transporting the equipment to and from the field sites, the generator was stored in a sealed green garbage bag in order to avoid any possible contamination from fumes into the air lines. Furthermore, before each day of measurements, all of the lines and surfaces would be carefully cleaned, rinsed, dried and sealed with Swagelock end caps or placed in clean polyethylene bags.

Collected air samples were stored in clean evacuated stainless steel electropolished canisters manufactured by Biospherics Research Corporation (Hillsboro, Oregon USA). Flow into the canisters was regulated by the 1 SLPM Tylan General mass flow controller and the second metal bellows pump. The canisters are approximately 4 litres in volume and are filled to a pressure of 200 kpa which provides ample volume for the laboratory analysis. The length of time required to fill the canisters was approximately 12 minutes at a flow rate of 1 litre per minute. Pressure inside the canister was monitored with a stainless steel pressure gauge (Matheson, Illinois USA)

A difficulty faced when measuring hydrocarbons is the possibility of contamination by anthropogenic hydrocarbons released from within the gas exchange system. For this reason the entire system was assembled using inert compounds such as Teflon, stainless steel or glass. Measurements were conducted prior to the field season in order to ascertain the extent of outgassing of contaminants from the tubing and sensors in the system. Prior to each day the equipment would be carefully washed or flushed with clean air. Analysis reveal that initially there were no significant contaminants released from the system. During the field measurements

however, some contamination was observed which will be discussed in the results and discussion section (chapter 3 & 4)

The bottom hemisphere of the glass cuvette rested in a Plexiglas bracket which was attached to a 3 metre long aluminum pole. This cuvette-boom assembly was then attached to a 4 metre mast supported by a large tripod which in turn was fastened to the ground with large spikes(see figure 2.4). Height of the boom could be adjusted relatively easily and the entire

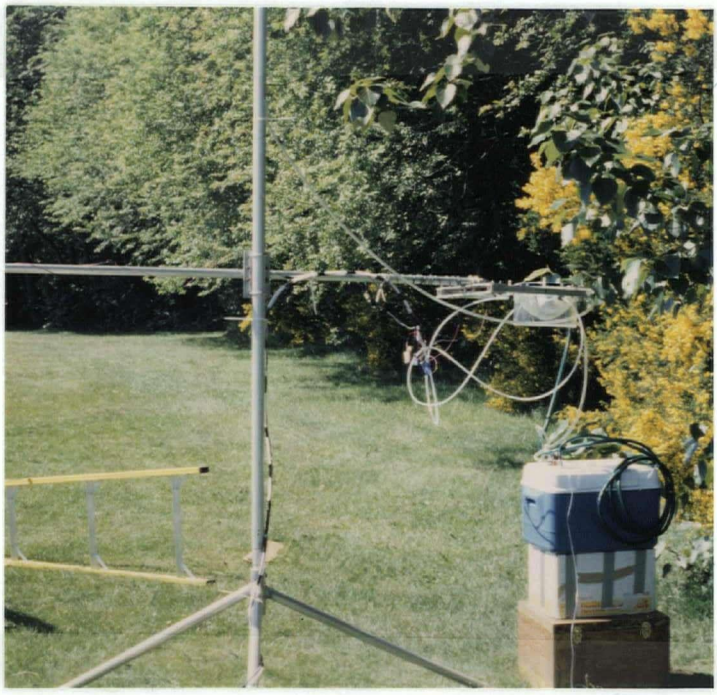

Figure 2-4 Cuvette attached to Mast Boom assembly. Picnic cooler is used for cooling water bath

cuvette-tower assembly could be moved by two people. With this system branches that were located up to three metres from the ground could be sampled

Once the canisters were filled they were shipped by air to the Center for Atmospheric Chemistry (CAC) Located at York University, Toronto, Ontario.

The Gas chromatograph used for this study was a Hewlett Packard Model 5890 II using a Flame Ionization Detector. This system has a custom built cryogenic enrichment device for

sample injection cooled to approximately -180°C. The chromatographic column is a DB-1, 100 metre long, 0.25mm I.D tube with a 0.25 mm film thickness manufactured by J&W Scientific Corporation. Column heating is programmed for -30°C for 1 minute followed by an increase of 4°C per minute to 288°C. The carrier gas is helium with a linear velocity of approximately 27 cm/sec. Chromatographic data is acquired using a 486 IBM clone personal computer and Hewlett Packard HP 3365 Chemstation software and interface. Data integration is done using the software except at dilute concentration where manual integration by the operator has been found to produce more consistent results. Accuracy of this GC system is conservatively estimated to be ± 10% for alkanes and ± 20% for other compounds. Precision of the system is typically ± 2% at concentrations above 0.1 ppbv. Below this concentration precision degrades. As a worst case, in portions of the chromatograph where separation is poor and concentrations are low, the precision is typically ± 20% for a set of three samples. Because of the retention characteristics in the capillary column, it is virtually impossible to obtain a meaningful measurement of the concentration of oxygenated compounds such as alcohols.

Samples were analyzed approximately two weeks after they were collected. The question of sample degradation over time has been addressed by Singh and Zimmerman (1992) among many others. Stainless steel canisters are a widely accepted method of collecting air samples and are used by many researchers. Some substances are not particularly stable in the canisters such as ethylene and acetylene. However, the compounds of interest such as isoprene and monoterpenes appear to be quite stable for extended periods of time (Byron Kieser, Personal communication).

2.2 Sampling strategy

In order to better understand the emissions of hydrocarbons from vegetation into the LFV airshed, those plant species which are the most important contributors must be examined in detail. The total quantity of hydrocarbon emitted by a particular species of vegetation in the region will depend on how much hydrocarbon the individual plant releases and the areal coverage of that particular species in the region. Information on emission rates of many different species has been compiled in the literature (e.g. Tanner et al, 1992, Evans et al. 1982, Zimmerman, 1981, Lamb et al. 1987, Lamb et al, 1993). Although these values will not necessarily be completely applicable to vegetation in the LFV because of local conditions and the unique environmental history, they do provide a rough guide to which species are likely to be strong VOC emitters

Based on the available resources (laboratory analysis costs and sampling time required) and knowledge of the vegetation in the lower Fraser Valley, four tree species were chosen for detailed study. These were Black Cottonwood (*Populus balsamifera ssp. trichocarpa*), Western Red Cedar (*Thuja plicate*), Coastal Douglas Fir (*Psudotsuga menziesii ssp. menziesii*) and Western Hemlock (*Tsuga mertensiana*). The Black Cottonwood was chosen based on the fact that it has been observed to emit isoprene at an extremely high rate (Tanner et al., 1992) and many fast growing tree species of the same genera such as trembling aspen and poplar are also known to emit large quantities of isoprene. Cottonwood is a rapid colonizer confined mainly to recently disturbed areas such as river banks and floodplains and so in terms of areal coverage is not one of the more common species in the LFV. However, it was felt that its probable high emission rate merited further investigation. The three coniferous species were chosen because they are extremely common throughout the area. Although values for their emission rates in the literature are not exceptionally high (Guenther et al., 1994, Tanner et al., 1992), their extensive

areal coverage would likely make these species relatively important contributors to the overall biogenic hydrocarbon emissions in the LFV. Since cottonwoods and related species are known to have high emissions of isoprene compared to the coniferous trees in the area, a conscious decision was made to focus more effort at sampling cottonwood to determine the temperature and PAR dependence of isoprene emissions. For the other three tree species, the light dependence of isoprene emissions was effectively ignored simply because there were not enough resources to sample at a wide variety of temperature and light conditions for all four tree species.

Some very limited sampling was done using the cuvette on other common plant species including blueberries (*Vaccinium uliginosum*, Northland variety), Japanese Knotweed (*Polygonum schalinense*), Red Alder (*Alnus rubra*) and blackberries (*Rubus ursinus*). Results from these measurements will be discussed Appendix 3.

2.3 Field sites

The study sites were located on the extensively forested University Endowment Lands (UEL) surrounding the University of British Columbia (Figure 2.5). The reason for conducting the study in this area include the large number of trees from which to sample, its location relative to the prevailing winds and the city of Vancouver and its close proximity to the laboratory. The built up areas of the university campus would best be described as suburban with relatively low building density and a large amount of vegetation. The rest of the UEL are composed of second growth coastal rain forest of approximately 80 years in age. The measurements were conducted during the summer of 1995 on warm sunny days which are usually characterized by sea breezes advecting relatively unpolluted air from the Straight of Georgia (Steyn and Faulkner, 1986). This

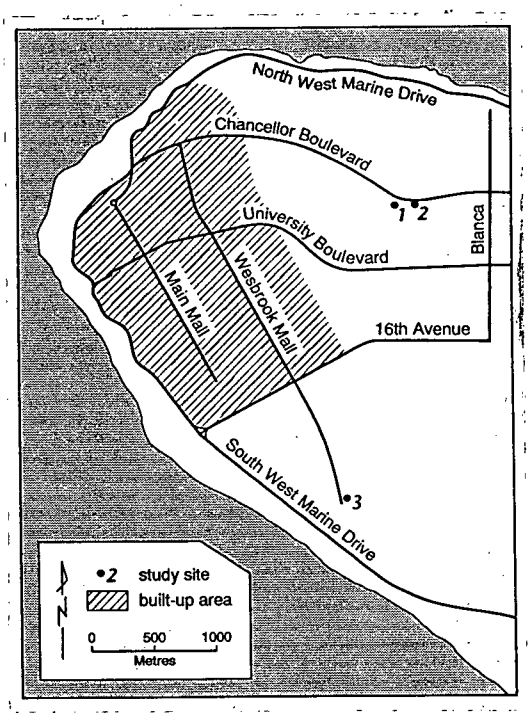

Figure 2-5: Location of trees sampled during 1995 field measurements. Sites 1 and 2 were cottonwood trees while site 3 had Western Red Cedar, Coastal Douglas fir and Coastal Hemlock. Built up area is predominantly suburban in nature with few significant anthropogenic VOC sources except light vehicular traffic. Non shaded area is heavily vegetated and composed primarily of 80 year old coniferous second growth forest

minimized the possibility of measurements being contaminated by a hydrocarbon rich plume from an extensive areal source.

The first criteria for choosing which tree to study was relatively easy access for the vehicle transporting all the equipment and that there were branches relatively close to the ground. Often in a closed forest canopy the first set of branches were located too high above the ground for measurements. For this reason all of the trees studied were at the edge of a forest canopy usually bounded by a cut grass surface, conditions which may not be completely representative of trees within the forest canopy. The second criteria was the tree had to appear healthy and not show any signs of moisture stress or disease. All of the trees sampled were quite large and so likely had extensive root systems. This fact coupled with the relatively wet summer (Figure 2.6) rule out the likelihood of any serious moisture stress during the measurement period. The third reason for choosing a particular tree was its distance from possible local sources of contaminants. Although the activated carbon filter was always used, the presence of anthropogenic hydrocarbons from car exhausts, buildings or other local sources was avoided as much as possible.

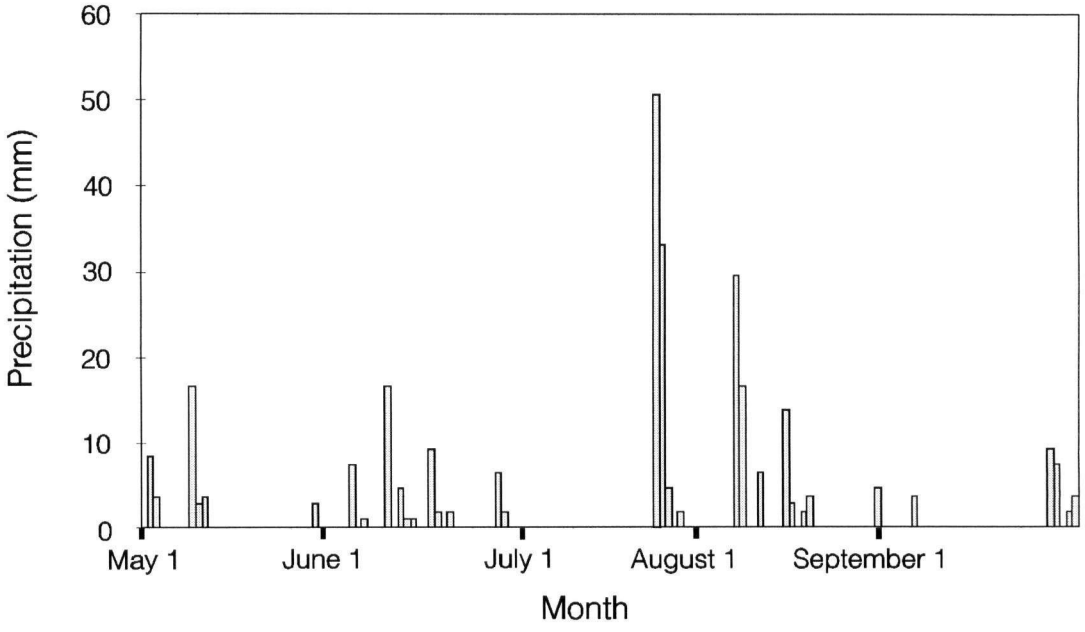

Figure 2-6 Daily total precipitation measured at the University of British Columbia climate station for summer of 1995.

2.4 Sampling Procedure

When a suitable tree was found, the equipment was placed approximately ten metres downwind of the tree. Total set up time for the equipment and testing was approximately 90 minutes before the first measurement. The bottom section of the cuvette was placed in its bracket underneath a suitable branch so the branch rested in the padded notch. Extreme caution was used sa as not to disturb the branch in any manner such as breaking the bark or having any leaves touching the sides of the cuvette. A very difficult problem encountered was the fact that tree branches tend to sway a considerable amount in even a light wind with cottonwoods being particularly difficult to control. In order that the branch was not torn free of the cuvette, a field assistant was required to hold the branch in place while it was being enclosed. The gas exchange system was then turned on allowing the flow controllers to achieve a steady value and to ensure that all systems were operating properly. When temperature and light conditions chosen for the test were achieved, the cuvette lid would be attached with its Plexiglas clamp. Air entering and exiting the cuvette was vented for approximately ten minutes in order to flush the lines. Following this the 2-way valve was opened starting the process of filling the canister.

While the canister was filling, temperature and photosynthetic radiation levels were monitored constantly to make sure they remained within the desired range. Temperature of the cuvette was controlled with the cooling water bath which could be operated both automatically or manually. Photosynthetic radiation was partially controlled by placing layers of cheesecloth over the cuvette. Since photosynthesis saturates for many plant species at approximately 1000 μmols of photons $m^{-2}s^{-1}$ (e.g. Taiz and Zeiger, 1991, Guenther et al., 1991, Jones, 1991), this was the maximum level desired during the field experiments. Photon fluxes in excess of this has little

effect on the rate of photosynthesis or light dependent isoprene production (Guenther et al, 1991, Sharkey et al., 1991) but would cause an unwanted increase in temperature.

After the first sample of the day, tests could be run approximately every half hour with a maximum of about 8 enclosure measurements per day. Upon completion of the enclosure experiments, the branches were clipped off, placed in a paper bag and labeled. At the end of the field season all the branches were dried in an oven at 105 °C for approximately 24 hours. For each branch the dry mass of green matter (leaves or needles), woody stems and other components (cones or berries) were measured on an analytical balance accurate to ± 0.001 grams.

Analysis of environmental data obtained was done as soon as possible after the measurements were taken in order to address any sensor or equipment problems that might have arisen. Results from the chemical analysis of the air samples were usually obtained a month after the collection of the sample. This delay made it impossible to know if a particular sample was being contaminated during its collection requiring extreme caution during the sampling in order to avoid this possibility. A total of 117 different chemical compounds were detected in some or all of the samples collected in quantities deemed significant. (usually greater than 0.01 part per billion). This agrees well with the findings of Singh and Zimmermann (1992) who found that there are approximately 100 species of non methane hydrocarbons that constitute most of the biogenic emissions.

3. Results

3.1 Environmental conditions during sampling

3.1.1 Photosynthetic photon flux density measurements

Examples of photosynthetic photon flux densities (PPFD) measured during the sampling are shown in Figure 3.1. Unfortunately there are some problems encountered when using this instrument for measurements of PPFD within a plant canopy. The first difficulty arises from the sensing element being a single disk with a diameter of approximately 5 mm. Within a plant canopy, photosynthetic radiation is extremely spatially heterogeneous because of shading from vegetation elements causing sunflecks and dappling. Thus, a single point measurement may not be representative of PPFD unless readings are averaged over a sufficient time period or spatial area. Even though the representativeness of a single point measurement in a canopy is somewhat questionable, every effort was made to place the PAR sensor in such a manner as to simulate conditions within the cuvette. In addition, the 10 to 15 minutes required for sample collection provided a reasonable length of time to allow temporal averaging and increased the representativeness of the measurement.

A second difficulty arises from the radiation sensor head being placed so that it is oriented parallel to the ground. This provides a standardized procedure for measurement of radiation impinging on a large homogeneous horizontal surface such as the top of a crop or forest canopy. However, this will not be able to adequately measure the radiation absorbed by an individual canopy element since branches and leaves can be oriented upright or drooping downwards. During air sample collection, the PPFD sensor orientation was adjusted using a small amount of plasticene so that it would be parallel to the leaves in the cuvette and thus be more representative of their PPFD. This problem was almost exclusively associated with large cottonwood leaves

which often sagged inside the cuvette because of their size. Figure 3.1a shows a relatively constant flux of photons at a density of approximately 1250 μmols m^2 s^{-1}. This is characteristic of fairly bright sunshine and is likely to provide ample energy for the light reactions of photosynthesis (Jones 1992). Figure 3.1b demonstrates a fairly common case where a high intensity of PPFD was achieved (approx. 1350 μmols m^2 s^{-1}) but shadows from overhead branches swaying in the wind shaded the sensor giving infrequent and short lived precipitous drops in PPFD. Figure 3.1c has a mean value of approximately 800 μmols m^2 s^{-1} but shows some lower frequency fluctuations caused by patchy shadows from cumulus clouds. Figure 3.1d shows a time trace of PPFD starting out with a relatively low level of radiation and then undergoing a switch to high levels of radiation with both regimes characterized by high amplitude high frequency fluctuations caused by movement of the sun combined with branch sway. During the first 400 seconds the sensor was located in a shadow of a branch and occasionally experienced bright sunlight. As the sun moved through the sky, the sensor became increasingly positioned in the sunlight experiencing some shadows, essentially reversing the pattern of the first 400 seconds. Most traces of PPFD during the 10 to 15 minute sample collection period are similar to figures 3.1a or 3.1b. In those cases where the sunlight was particularly intense (greater than 1300 μmols m^2 s^{-1}) cheesecloth was placed over the cuvette and sensor to reduce radiation intensity below saturating levels for photosynthesis.

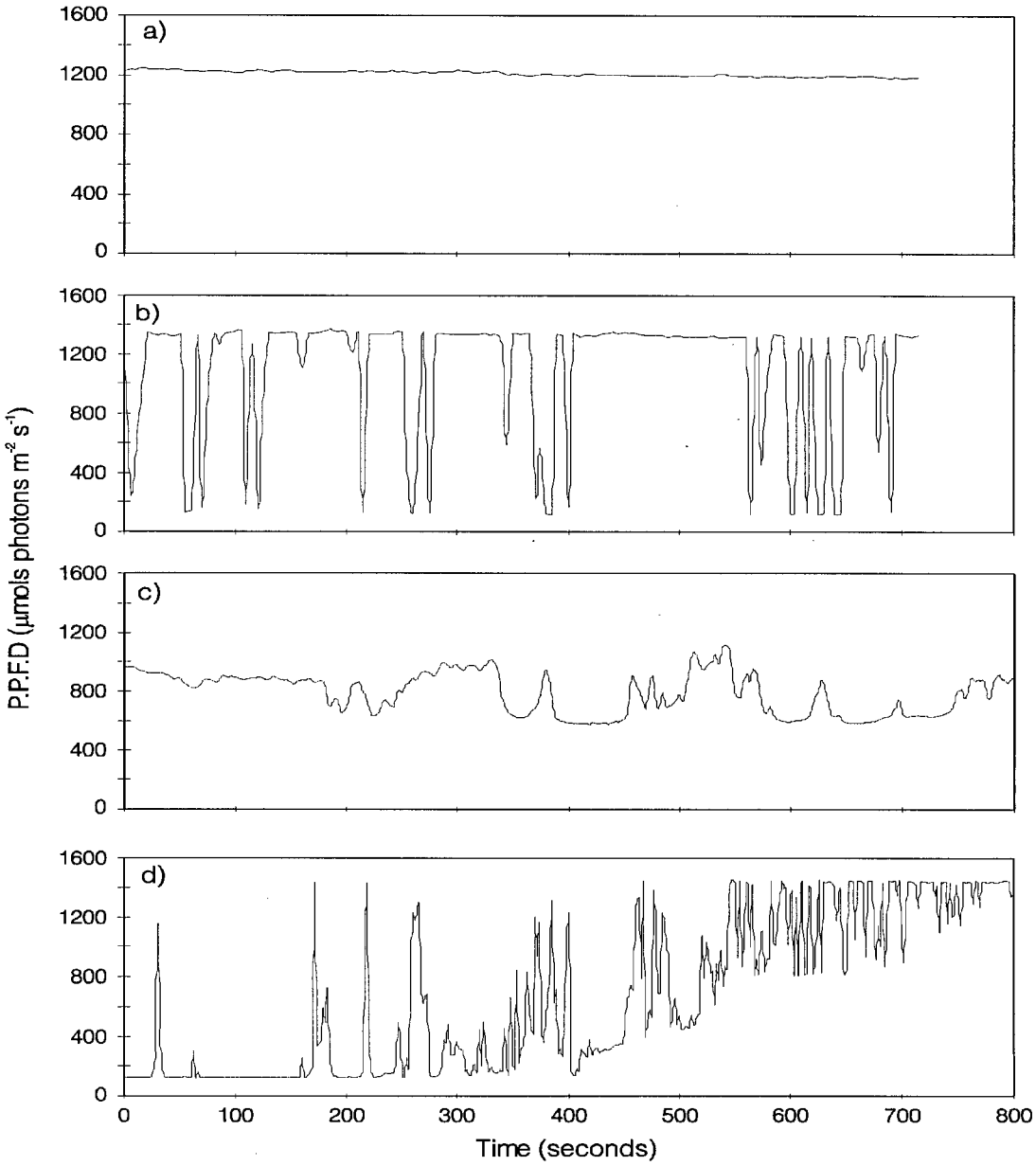

Figure 3-1: Examples of photosynthetic photon flux density for a) constant radiation intensity and highly variable PPFD caused by branch shadows (b and d) or patchy clouds

3.1.2 Temperature measurements

Figure 3.2 demonstrates typical traces of branch temperature (obtained from both inside and outside the cuvette) over the sample collection period. Most notable is that inside branch temperature shows less short term variability compared to outside branch temperature. The variability of the outside measurements is a result of turbulent sensible heat flux from the ground while the significantly lower variability of temperature measurements inside is due to the large

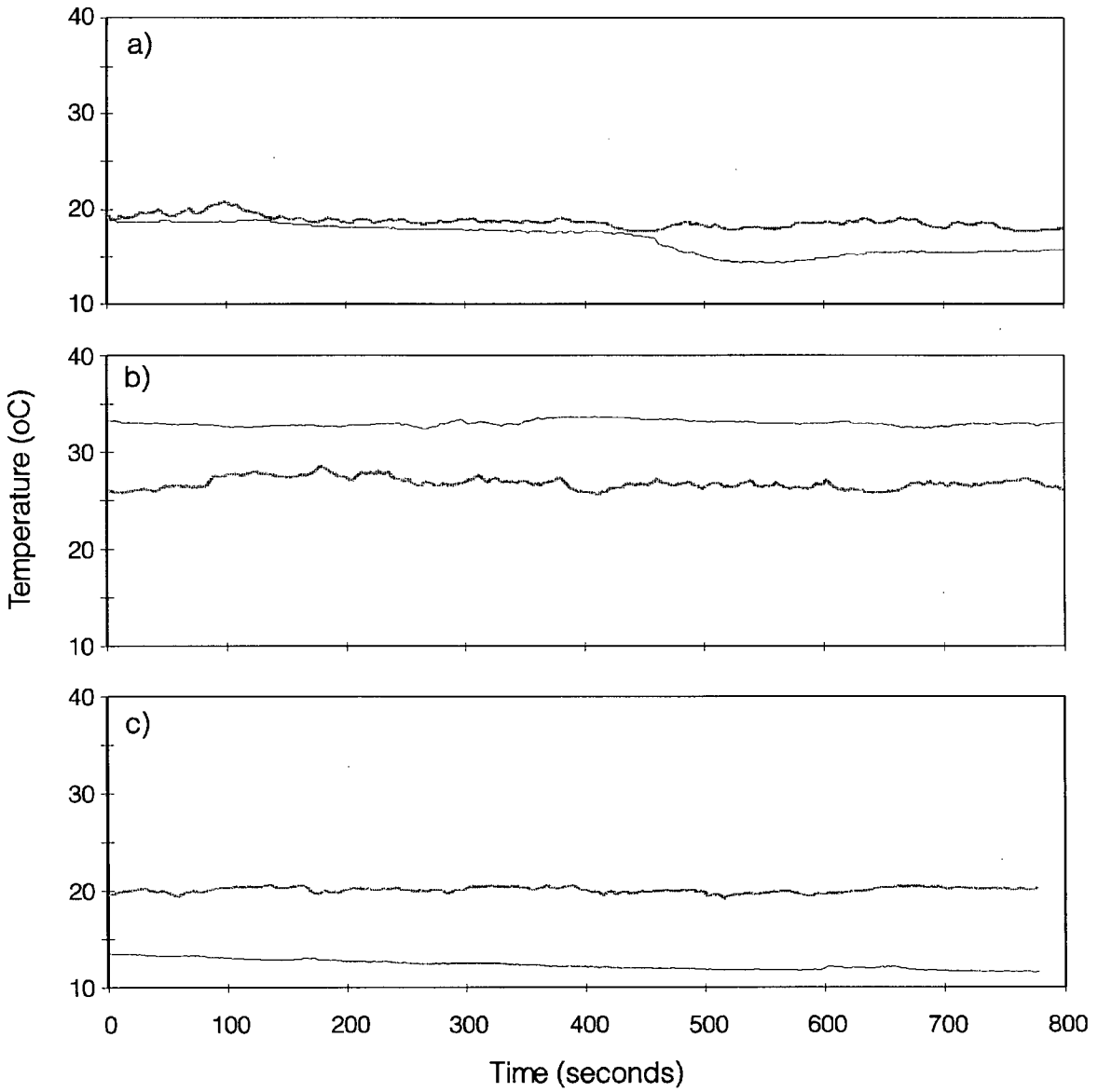

Figure 3-2: Examples of temperature traces observed for inside (thin line) and outside (thick line) branch temperatures during enclosure trials.

thermal mass of the enclosure system and its relatively slow response to forcing factors (such as changes in solar radiation or responding to the cooling system). Figure 3.2a demonstrates branch temperature inside the cuvette experiencing a 3°C decline starting at 450 seconds caused by the cooling system being activated shortly before. Figures 3.2b and 3.2c show examples of temperature traces in the case of high temperature and low temperature respectively.

In order to gain an understanding of the relationship between VOC emission to temperature, emission measurements must span a reasonable range of temperature conditions. Since these VOCs are precursors for photochemical smog, the range of temperature was decided to be that which is typically experienced during summertime ozone episodes. Most of the literature (e.g. Monson et al., 1992, Loretto and Sharkey, 1990, Juuti et al., 1990, Tingey et al., 1980) provide results for enclosure measurements obtained up to approximately 40°C. Summertime cloudless conditions in the Lower Fraser Valley can generally experience air temperatures ranging from a minimum of 10°C just after dawn up to approximately 30°C during the day. Sensible heat flux combined with evapotranspiration make leaf temperatures higher than 40°C rare (Spronken-Smith, 1994). Figure 3.3 is a plot of average temperature inside the cuvette against average temperature outside the cuvette for all enclosure measurements conducted during the summer of 1995. Obviously the best result would be all points falling on the 1:1 line so that branch temperature inside mimics exactly that of outside branch temperature ensuring no artificial temperature stress is placed on the enclosed branch by the cuvette. However, in many of the samples collected this was not the case since it was very difficult for a branch to achieve very warm or very cool temperatures naturally within the time constraints of the field project. In these situations the cuvette was used to intentionally modify branch temperature accounting for these large deviations from the 1:1 line in figure

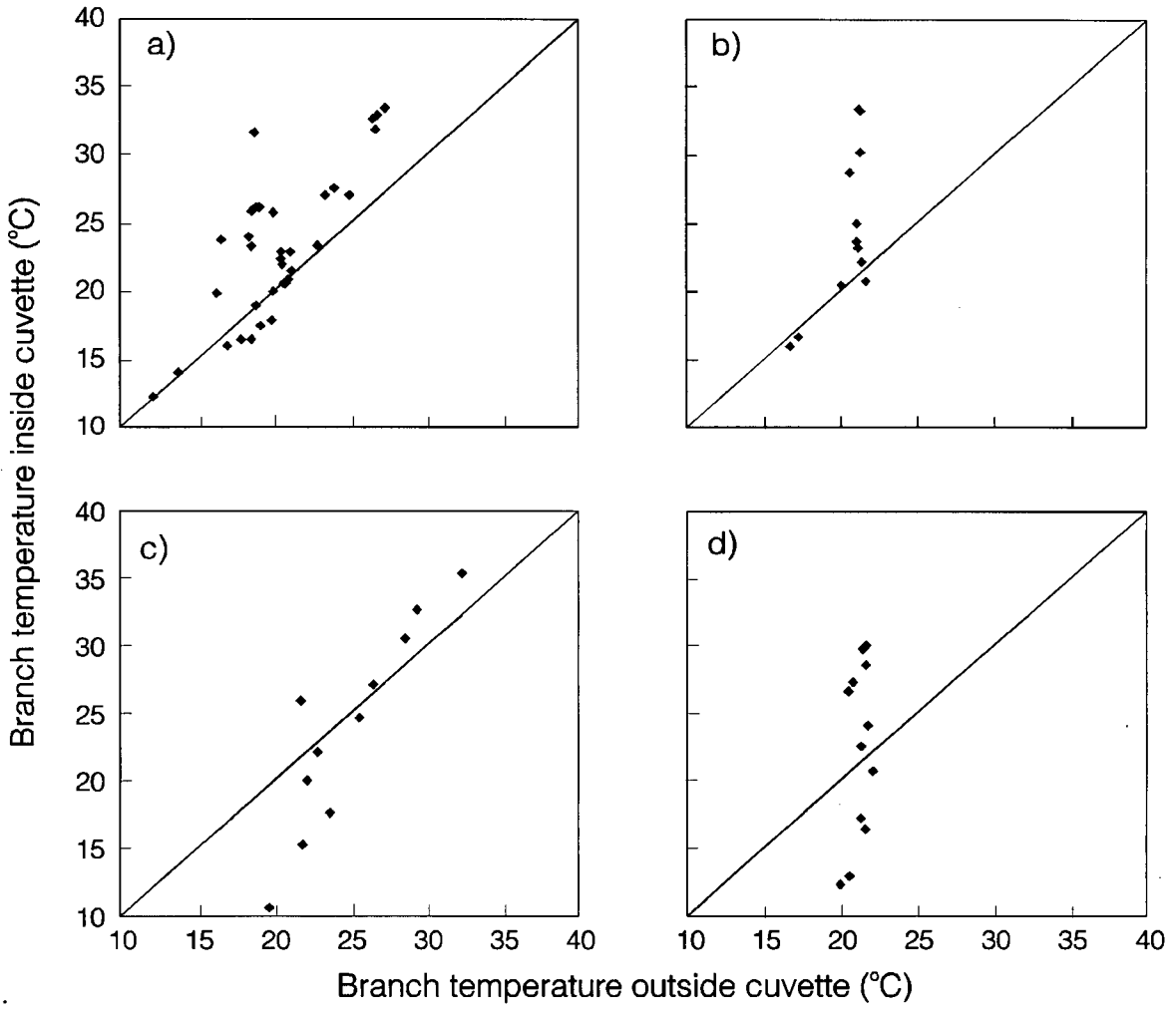

Figure 3-3: Plot of branch temperature inside cuvette vs. branch temperature outside cuvette for a) Cottonwood, b) Cedar, c) Douglas fir and d) Hemlock.

3.3. The physiological effect of an enclosed branch being a considerably different temperature than the rest of a plant is unknown but is likely to introduce some error in branch emission rate. This is an unfortunate reality of field studies where complete experimental control is very difficult to achieve

3.1.3 Carbon dioxide drawdown measurements

Photosynthesis rate was monitored during sample collection to ensure normal plant behavior (i.e. that it was in fact photosynthesizing). A single CO_2 detector was used to alternately sample air entering and air exiting the cuvette at thirty second intervals. Figure 3.4 shows some

typical outputs from the CO_2 detector. Calculations of average CO_2 assimilation during each 30 second interval used the last twenty seconds of data in order to allow the system to flush out the previous sample air. In figure 3.4 the traces of CO_2 are not normalized by amount of vegetation within the cuvette so that plots with greater step sizes are not necessarily experiencing greater rate of photosynthesis. During the first two days of sampling a problem with the CO_2 monitoring system was observed where concentration of CO_2 entering the cuvette would deviate greatly from normal ambient concentrations (see figure 3.4A). The reason for this fluctuation was finally isolated to outgassing of CO_2 from the charcoal filter. In some of the early samples collected, CO_2 concentration within the cuvette achieved values approaching double that of ambient concentrations (700 compared to approximately 360 ppmv). Studies by Loretto and Sharkey (1990) have shown that enriching a plant's atmosphere with CO_2 can cause isoprene emissions to increase significantly. Work by Guenther et al., (1993), has shown that changes in CO_2 concentration of the same order experienced in this experiment typically result in a 10 to 30% decrease in isoprene emission rate for Eucalyptus leaves. Sharkey et al., (1991), observed Oak leaves to emit more isoprene when grown in a CO_2 enriched atmosphere while Aspen leaves experience a decrease in isoprene emissions at higher than ambient CO_2 concentrations. It appears that without extensive laboratory chamber measurements, the relationship between CO_2 concentrations and emission rate for an individual plant species will remain unknown. The problem of outgassing was solved by simply placing the filter in a cool shaded container. The average rate of photosynthesis observed for all the different plant species ranged in values of 0.05 milligrams of carbon per gram dry weight per hour up to approximately 2 mgC g^{-1} h^{-1}. Almost invariably the coniferous species sampled demonstrated relatively low rates of carbon assimilation (Maximum 0.5 mgC g^{-1} h^{-1}) while the minimum assimilation rate observed by the cottonwood measurements was only slightly less than 0.5 mgC g^{-1} h^{-1}.

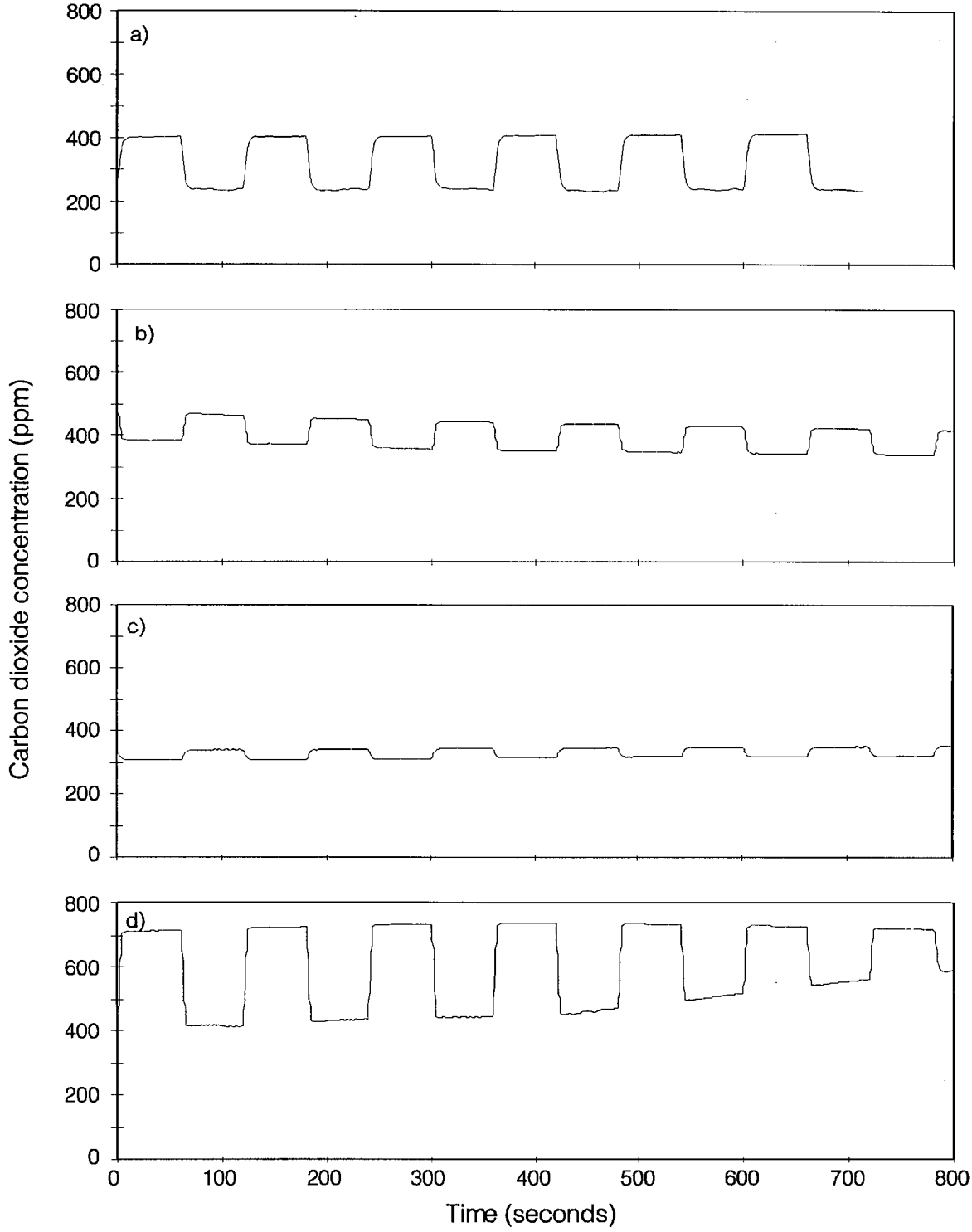

Figure 3-4: Example of CO_2 analyser measurements during enclosure trials. Note the fairly large deviation of ambient concentrations from 360 ppmv in plot d (See text for details).

3.2 Raw Hydrocarbon Data Results

Figure 3.5 shows two sample chromatograms obtained from laboratory analysis of air samples collected during this study. These are plots of signal outputs from the Flame Ionization

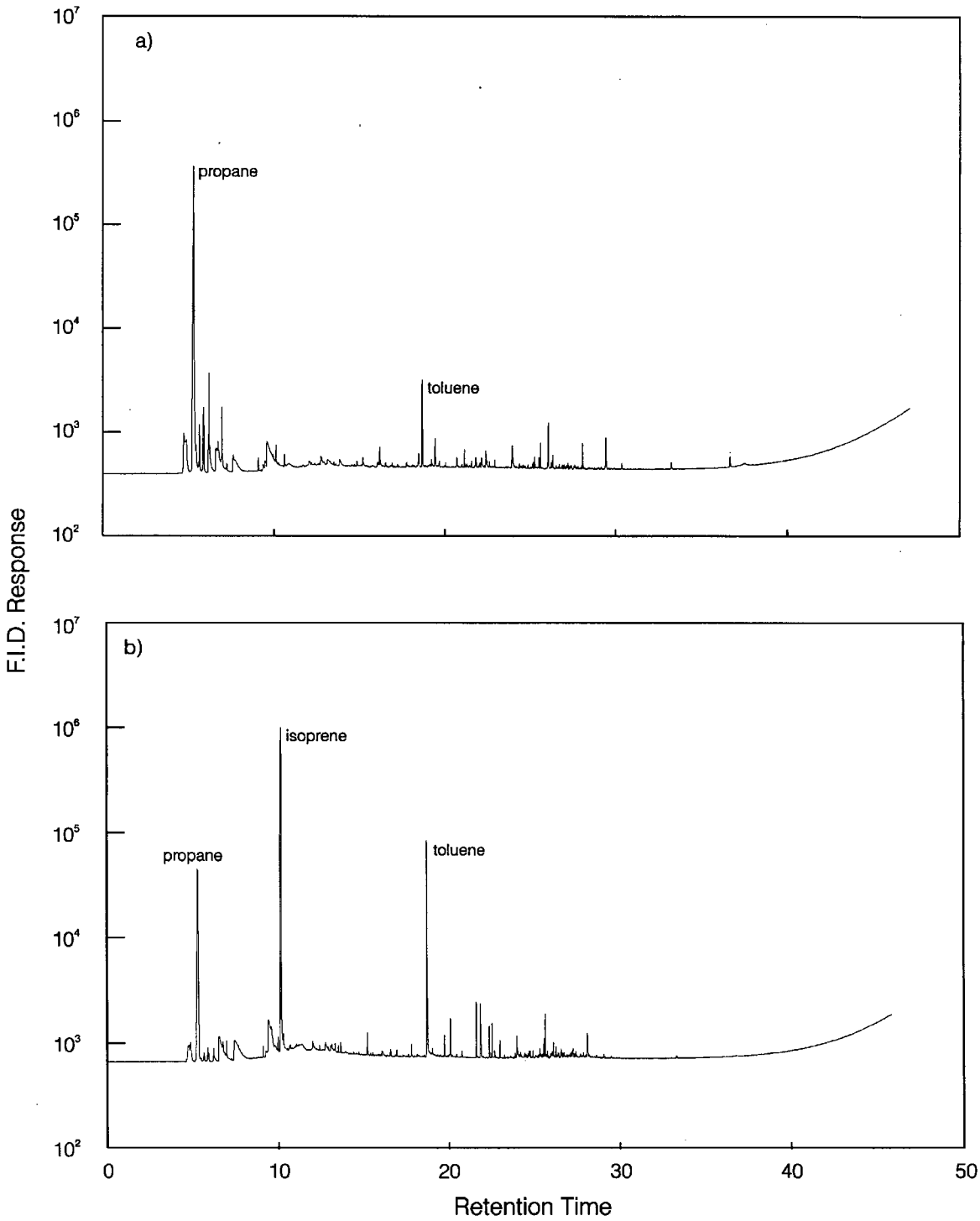

Figure 3-5a: Examples of GC-FID chromatograms obtained for typical (a) cedar and (b) Cottonwood air samples.

Detector (FID). Each peak represents an individual compound in the air sample with the amount of carbon within that particular compound passing through the detector being proportional to the area under the peak. This information is then converted to mixing ratio or volume concentration with units of parts per billion. Implicit in this data analysis is that every component behaves as an ideal gas.

Figure 3.6 shows a bar graph of the various concentrations of compounds observed in the three chromatograms in figure 3.5. Immediately noticeable is the huge range of hydrocarbon concentrations measured (See appendix 2 for a listing of compounds). Values as low as 0.01 ppbv were observed in most samples for a large assortment of hydrocarbons although the accuracy of measured concentrations this low is poor. Maximum values were on the order of 100 ppbv, and were usually observed for a very limited number of compounds. Some compounds occurred in high concentrations in many of the samples collected indicating either a large emission rate or contamination within the gas exchange system. Commonly occurring substances included (but were not limited to) isoprene (from cottonwood samples), 1-pentane, ethane, ethylbenzene, propane, propene and toluene. Each chromatogram was examined individually to determine the presence of anthropogenic contaminants. Any substance that occurred at unreasonably high concentrations, and was likely from an anthropogenic source, was omitted from the sample during further analysis. This is a very subjective procedure since it assumes definitive knowledge of which compounds are biogenic and which are not. Only toluene, propane and propene occurred consistently at concentrations high enough to indicate likely contamination and so were omitted from all sample analysis. Occasionally other substances such as ethylbenzene, isopropylbenzene and n-butane would also occur at relatively high concentrations and were thus omitted from further analysis of those particular samples. Singh et al., (1992) suggested an unknown global source of propane which could possibly be attributed to vegetation. In this analysis however,

concentrations of propane and propene were in many cases hundreds of times greater than all other hydrocarbons combined and so were assumed to be due to external contaminants. Since propane and propene are relatively unreactive in ozone forming photochemical reactions, neglecting them will have little effect on an emissions inventory of compounds that do react in photochemical processes. Toluene was another hydrocarbon which occurred at consistently high concentrations and was completely unexpected from vegetation. Attempts to isolate a source of toluene (by collecting air samples with no enclosed branch) revealed that it was being released from within the gas exchange system. However, these same "blank" tests often revealed relatively low concentrations of propane and propene indicating a possible biogenic source of these compounds. Owing to the substantial cost of analyzing these air samples, it is simply not feasible to collect a large number of samples in order to isolate the source of some contaminants, especially since they occur at concentrations so low as to not interfere with identification of other compounds. It is therefore entirely possible that some vegetation species examined in this study are sources of hydrocarbons such as propane or propene. Compounds which are anthropogenic contaminants but were not excluded will likely be relatively unimportant because of their very low concentrations.

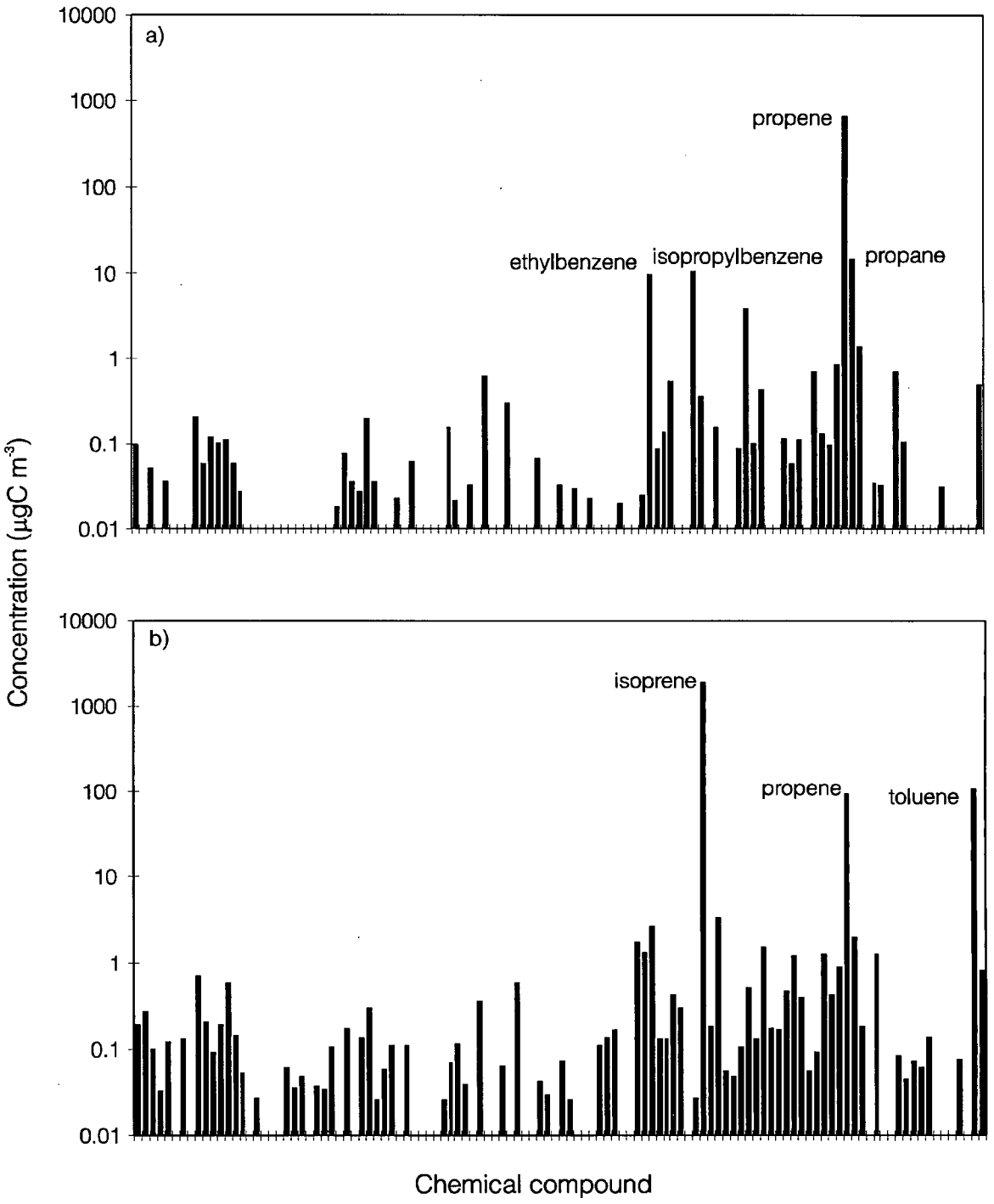

Figure 3-6: Hydrocarbon concentrations (µg m^{-3}) obtained from chromatograms in Figure 3.5.

3.3 Branch emission results

Calculations of flux of a particular hydrocarbon from an enclosed branch is demonstrated in equation 2.1 and 3.1. The first step is to convert the volume of hydrocarbon per volume of air into a mass of hydrocarbon per volume of air. At 0°C and a pressure of one atmosphere (conditions at which the mass flow controllers are calibrated), the volume of air occupied by one mole of an ideal gas is given by the ideal gas law in equation 3.1

$$\frac{V}{n} = \frac{RT}{P} \qquad (3.1).$$

where P is pressure in Pascals (kg m^{-1} s^{-2}), V is volume (m^3) n is number of moles (in this case 1) and T is the absolute temperature (Kelvin). Dividing concentration of any particular hydrocarbon (ppbv) by this number yields the number of moles per cubic metre of that particular compound which is then multiplied by the number of carbon atoms in that compound and the GMW of carbon the yield the concentration in μgC m^{-3}. This is then substituted into equation 2.1 yielding biogenic VOC emission rate from a branch with units of μgC g^{-1} h^{-1}.

Figures 3.7 to 3.10 shows the relationship between hydrocarbon emission rate and temperature for the four different tree species. The data y-axis (emission rate) is scaled logarithmically since the vapour pressure-temperature relationship and the activity of enzymes with temperature are both exponential relationships. If either of these processes control hydrocarbon production or emission, then it is reasonable to expect emissions to also demonstrate an exponential relationship with temperature. Another reason for the logarithmic y axis scaling is the extremely large range in emission rates both within and among the different tree species sampled. Difference in emission rate between all tree species spans almost five orders of magnitude while difference in emission rate within a species generally spans two orders of magnitude making comparison much easier when compressed on a logarithmic scale.

The relationship between emission rate and temperature (and P.A.R. for isoprene) was analyzed using linear regression with the least squares best fit line and the 95% confidence intervals shown on each plot. The natural logarithm of the emission rate was assumed to be directly related to the two (assumed) independent variables temperature and P.A.R. as done in Tingey et al, (1980), Juuti et al, (1990) and Lamb et al., (1985). This yields a simple log-linear relationship given in equation 3.2

$$\text{Emission Rate} = \exp(\text{const} + B_1 \times T + B_2 \times \text{PPFD}) \qquad (3.2)$$

Where temperature T has units of °C and P.A.R. has units of μmols m^{-2} s^{-1}. In the case of the log linear model to predict monoterpene or other VOC emission rates, it was assumed that B_2, the light dependence factor, was equal to 0. Table 3.1 provides summary information for each of the four samples.

Use of this general linear model requires a number of assumptions which in some cases have not been strictly met in this study. The first assumption is that the data consists of randomly selected independent samples. Unfortunately due to the constraints of the apparatus, it was not possible to reach very high into the plant canopy so that all samples were biased towards the lower sections of the trees. Furthermore, since there was only a limited number of branches that were suitable for sampling at a particular tree, branches were oftentimes sampled more than once violating the assumption of independence. This can be justified by the fact that the cuvette is designed and implemented in order to minimize any stress on the branches. Any branch that was resampled on a particular day was removed from the cuvette for at least an hour in order to allow it to "rest" from any imposed stress from previous sampling. Usually the sampling during the day would progress from cooler morning temperatures to the warmer afternoons. If there were any physiological damage to the branches it would be expected that isoprene emission would be much less well behaved than they were (see figure 3.7). With these precautions, it is not unreasonable

to assume that the branch had no "memory" of previous testing that would affect the results. Another problem in the sampling methodology was the fact that all the trees sampled were adjacent to cleared grassy areas (for ease of access) which will undoubtedly affect the microclimate of the trees and may introduce a bias in the results.

isoprene		Constant		Temperature		P.A.R.		
	n	coeff	Pvalue	coeff	Pvalue	coeff	Pvalue	Model R^2
Western Red Cedar	12	-8.434	0.000	0.115	0.000			0.816
Cottonwood	34	-2.707	0.003	0.181	0.000	0.002	0.001	0.661
Douglas fir	11	-4.491	0.000	0.090	0.002			0.668
Hemlock	12	-7.630	0.000	0.120	0.000			0.801

monoterpenes		Constant		Temperature		
	n	coeff	Pvalue	coeff	Pvalue	Model R^2
Western Red Cedar	12	-0.564	0.002			
Cottonwood	33	-4.525	0.000			
Douglas fir	11	-3.445	0.009	0.137	0.009	0.547
Hemlock	11	-2.064	0.000			0.000

Other VOC's		Constant		Temperature		
	n	coeff	Pvalue	coeff	Pvalue	Model R^2
Western Red Cedar	12	-3.691	0.000			
Cottonwood	34	0.278	0.046			
Douglas fir	11	-1.852	0.036	0.076	0.033	0.413
Hemlock	12	1.685	0.000	-0.084	0.000	0.814

Total VOC's		Constant		Temperature		
	n	coeff	Pvalue	coeff	Pvalue	Model R^2
Western Red Cedar	12	-0.497	0.004			
Cottonwood	34	-0.733	0.241	0.160	0.000	0.546
Douglas fir	11	-1.866	0.054	0.107	0.011	0.528
Hemlock	12	1.645	0.000	-0.073	0.000	0.776

Table 3-1: Results of linear regression analysis of four tree species. n is the number of samles, The constant coefficient is the intercept of the log transformed emission rates (at T = 0) while the temperature coefficient is the slope of the regression line

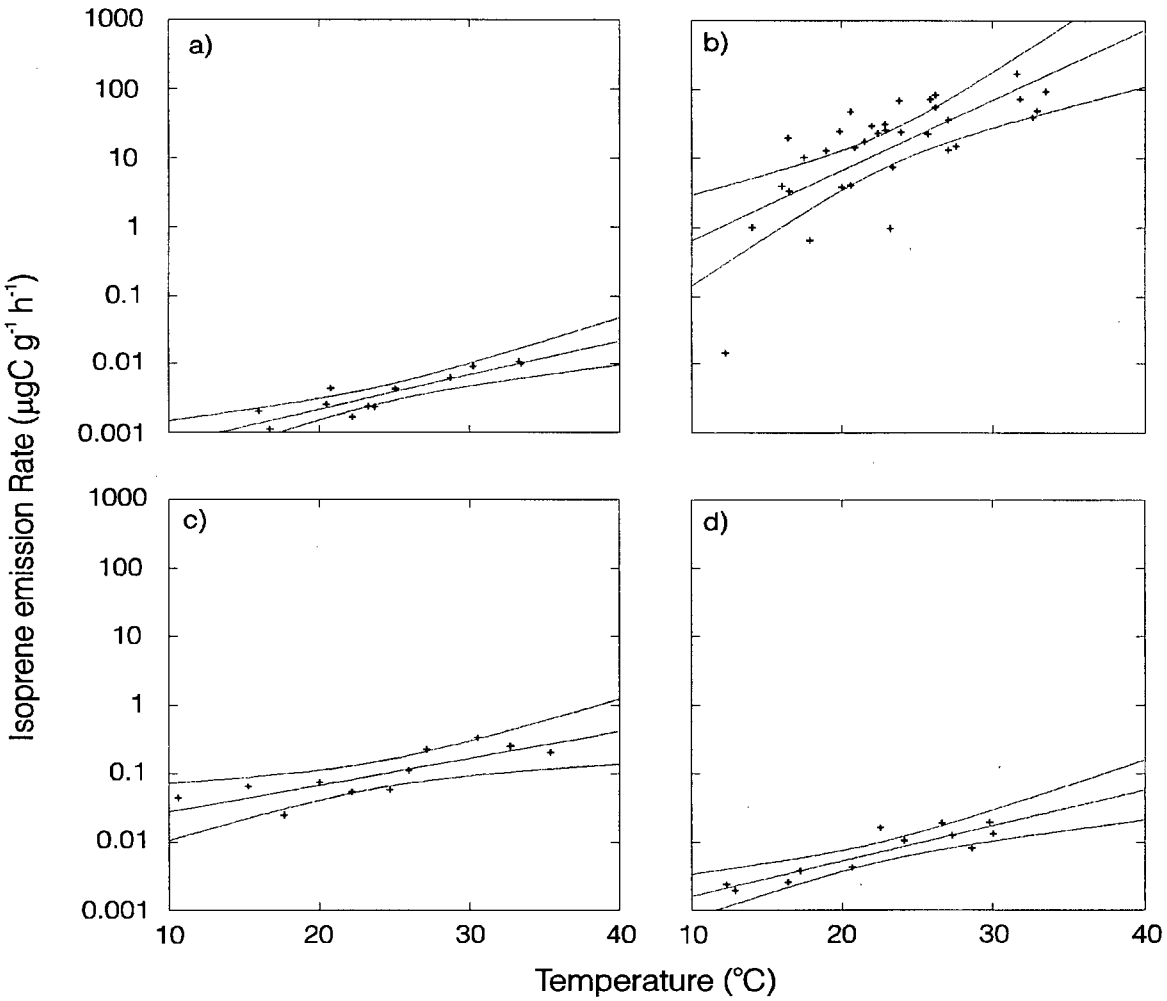

Figure 3-7: Isoprene emission rate observed from a) Western Red Cedar b) Black Cottonwood c) Coatal Douglas fir and d) Coastal Hemlock at a range of branch temperatrues. Curved lines indicate 95% confidence intervals.

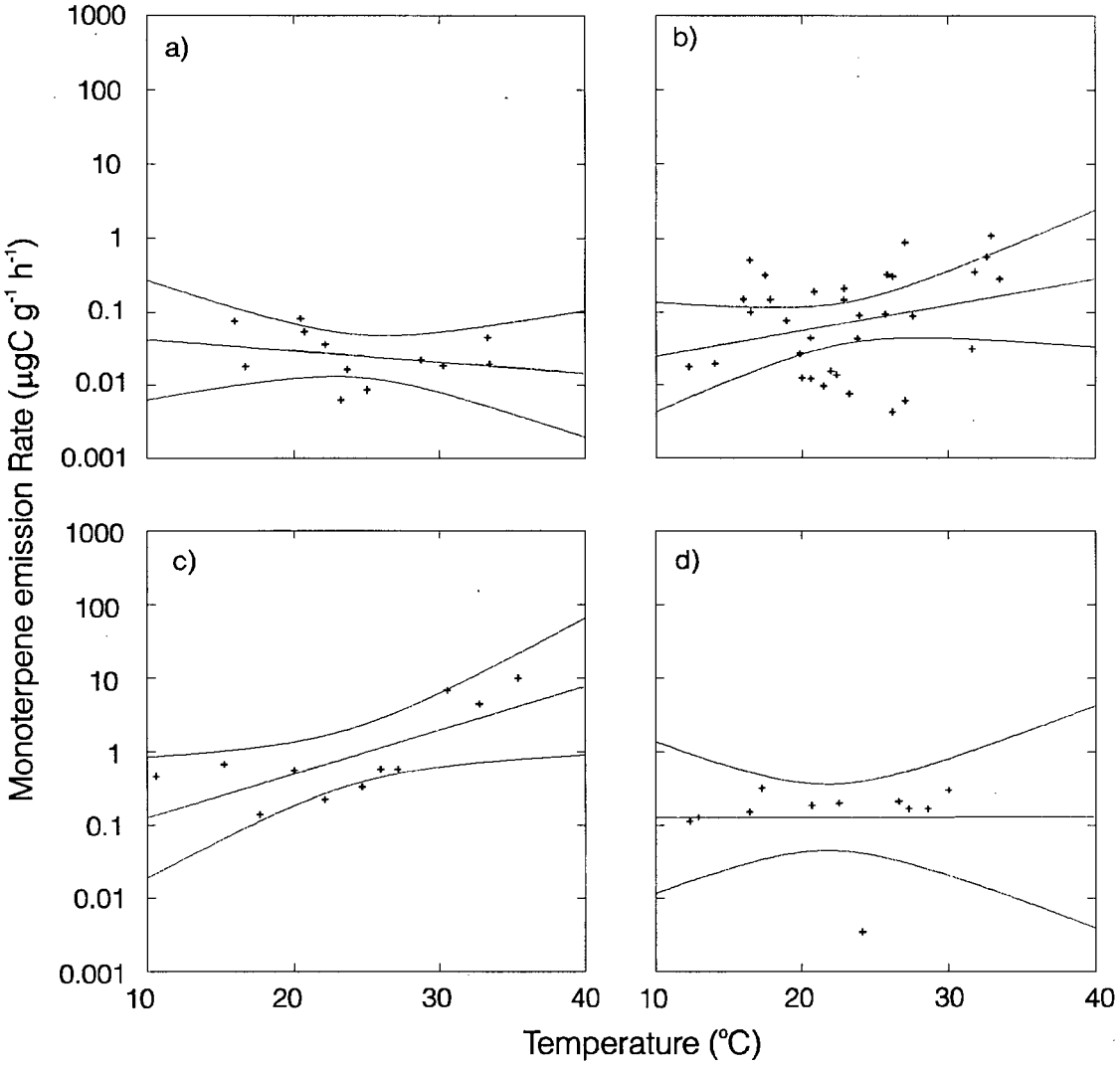

Figure 3-8 Monoterpene emission rate observed from a) Western Red Cedar b) Black Cottonwood c) Coatal Douglas fir and d) Coastal Hemlock at a range of branch temperatrues. Curved lines indicate 95% confidence intervals.

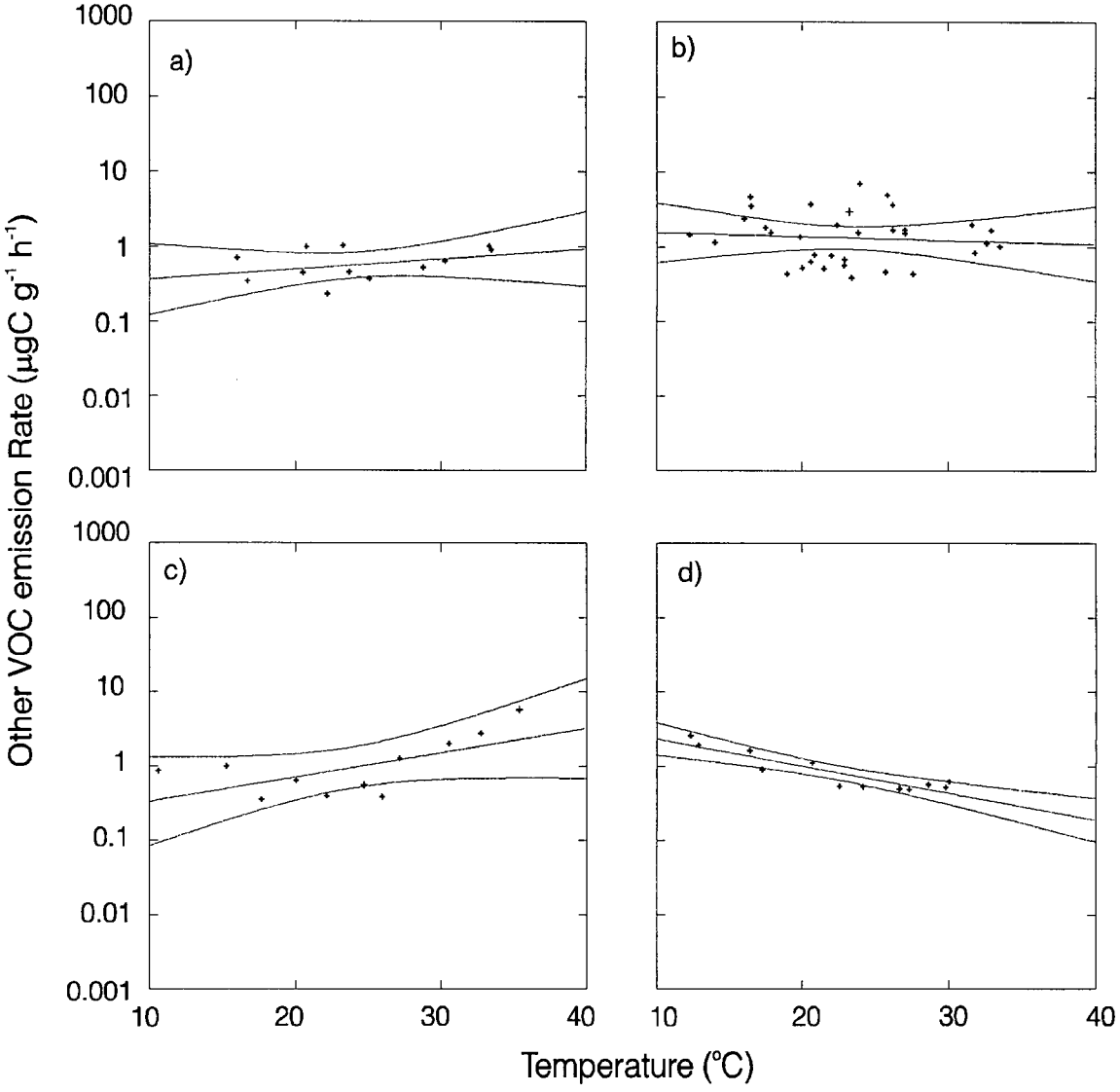

Figure 3-9 "Other' VOC emission rate observed from a) Western Red Cedar b) Black Cottonwood c) Coatal Douglas fir and d) Coastal Hemlock at a range of branch temperatrues. Curved lines indicate 95% confidence intervals.

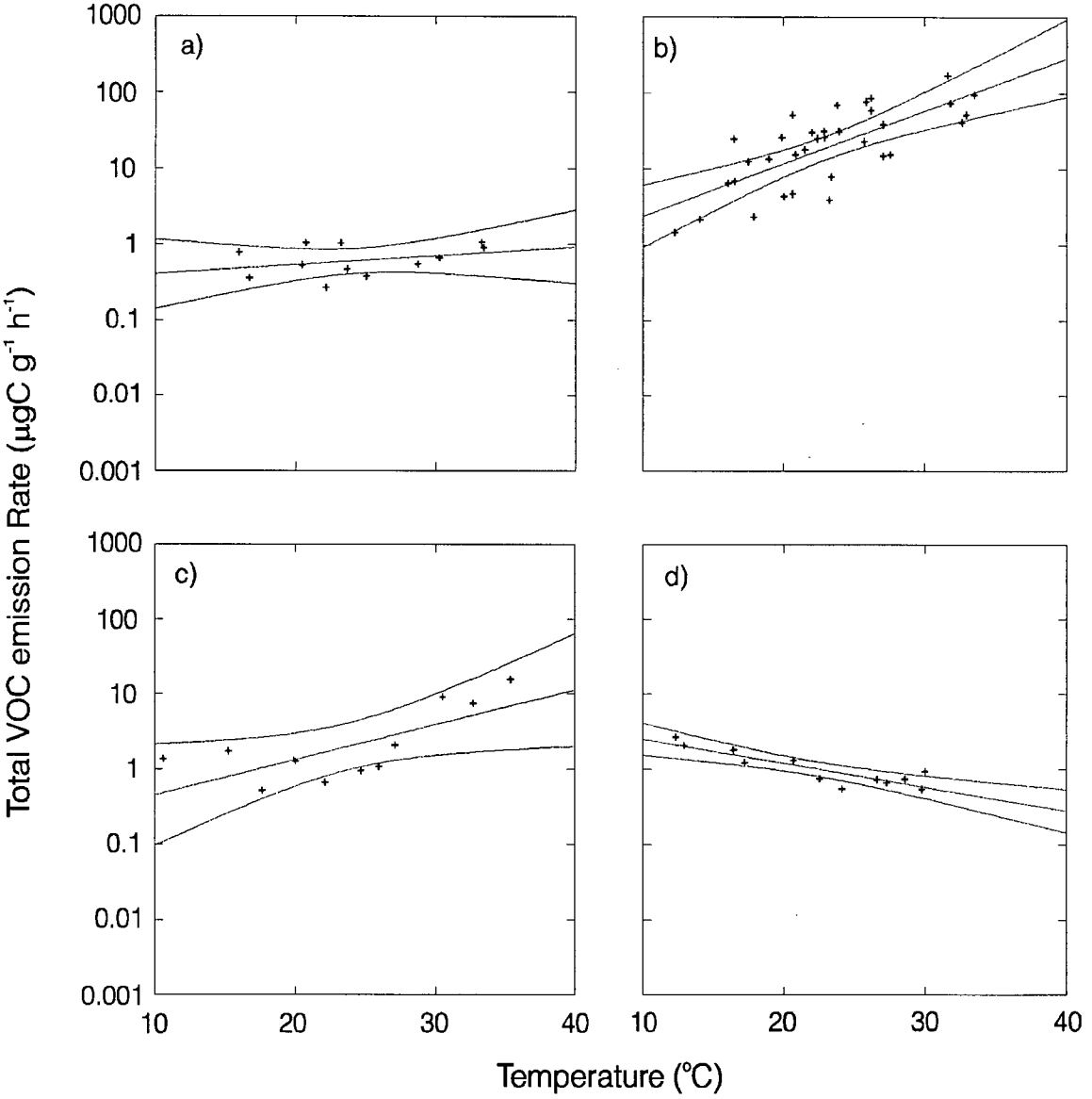

Figure 3-10 Total VOC emission rate observed from a) Western Red Cedar b) Black Cottonwood c) Coatal Douglas fir and d) Coastal Hemlock at a range of branch temperatrues. Curved lines indicate 95% confidence intervals.

Another factor that must be considered in this data analysis is interdependence between the temperature and P.A.R. measurements. Simply stated, these two variables are not independent but rather are highly correlated. The small number of samples obtained for the three coniferous species did not allow a relationship between isoprene emissions and light and temperature to be established. The Cottonwood tree was much more carefully investigated and it was possible to obtain measurements during periods when temperatures were cool but photosynthetic radiation was fairly high (clear mornings) or when temperatures were very warm but photosynthetic radiation was low (cloudy days).

Figure 3.7 shows emission rate of isoprene as a function of temperature for all four tree species. Notable is the high rate of emission from Cottonwood samples compared to the other species. Another feature is the remarkably small amount of scatter in isoprene emission rate for all four tree species as seen in both figure 3.7 and in the relatively high values of R^2 in the results of the regression analysis (table 3.1). All of the species examined show a statistically significant increase in emissions with increase in temperature ($\alpha = 0.05$). Note that the statistical significance of the constant coefficient is meaningless since the emission data are log transformed.

For the Cottonwood case, there is a data point that appears to be a far outlier from the main group of emission rates even though it is at the extreme lowest temperature and PPFD sampled (12.3°C, 73.2 μmols m^{-2} s^{-1}). This outlier could be a result of measurement error or it could be indicative of a threshold where isoprene emissions do not start in the daytime until a certain set of conditions have been achieved. This "threshold" behavior for isoprene emissions has been observed in enclosure measurements obtained from Aspen trees during the BOREAS study (Byron Keiser, Personal communication). However, with only one data point at this lower end of temperature and PPFD it is impossible to say with any certainty why this measurement is so low.

The emission of monoterpenes (α-pinene, β-pinene, limonene and myrcene) demonstrated considerably more scatter in the data than for isoprene emissions (see figure 3.8). Contrary to what one would expect from our conceptual understanding of volatilization of these substances, emission rate of monoterpenes is not related to temperature at $\alpha = 0.05$, undoubtedly because of the lack of sufficient data. There is a relatively large number of cottonwood samples yet again there is no significant relationship between terpene emissions and temperature at the 95% confidence level. Because emissions of isoprene were relatively well behaved and branch damage was avoided, this behavior for monoterpenes is quite puzzling. Hemlock samples also showed no significant relationship with temperature. As well, for the Hemlock measurements, there is a distinct outlier of extremely low monoterpene emissions which also cannot be easily explained. If a branch was physically damaged by the enclosure apparatus, an outlier that shows a much higher emission rate would be expected unless of course that all samples except the outlier in this case were excessively disturbed, an unlikely scenario.

The only species whose monoterpene emissions behaved as expected is the Douglas fir. It shows a statistically significant increase in emission rate with temperature and shows a model R^2 of 0.547. It is somewhat surprising that even with a small sample size this could be established while cottonwood show no significant relationship with n=33 (in one of the 34 Cottonwood samples no monoterpenes were detected). The amount of scatter observed from these measurements appears to be much greater than that in other studies in the laboratory (for example see Yokouchi et al, 1984, Juuti et al., 1990). However, Tingey (1981) noted the large amount of scatter observed in field studies and discussed the difficulty establishing a temperature-emission relationship for monoterpenes. Hov et al., (1993), also found very little relationship between many temperature and humidity parameters and the concentration of terpenes in a forest canopy.

The emission rate of VOCs grouped in the "other" class are shown in figure 3.9. As for monoterpene emissions, only Douglas fir shows a statistically significant increase in emissions as expected. Hemlock samples show a statistically significant decrease in emissions with increasing temperature while Cedar and Cottonwood samples show no significant relationship between the "other" VOC emissions and temperature.

When all three different hydrocarbon species are grouped together, Cedar emissions show no significant relationship with temperature even though one of the three classes (isoprene) does show a relationship. This simply indicates that the absolute amount of isoprene compared to total hydrocarbon emission rate of cedars is relatively small. Hemlock samples show a statistically significant negative relationship with temperature, again the significant positive relationship of isoprene emission with temperature is lost since it makes up only a small amount of the total hydrocarbon emissions. Cottonwood samples show a significant increase in total hydrocarbon emission with increasing temperature as a result of the large proportion of total emissions being comprised of isoprene. Douglas fir also shows a statistically significant positive relationship between emission rate of total hydrocarbons and temperature. Although the amount of isoprene is relatively small, the monoterpenes and other VOC emissions were relatively well behaved compared to other coniferous species and so total VOC emission rate demonstrated a positive relationship, with temperature.

Emissions of isoprene are known to be closely linked to the intensity of photosynthetic radiation because of the transduction of energy from the photosystems to the isoprene synthesizing apparatus. Only the cottonwood samples demonstrated any significant relationship with PPFD at the $a = 0.05$ level. (see figure 3.11). All other samples showed no significant relationship likely as a result of the small number of data points.

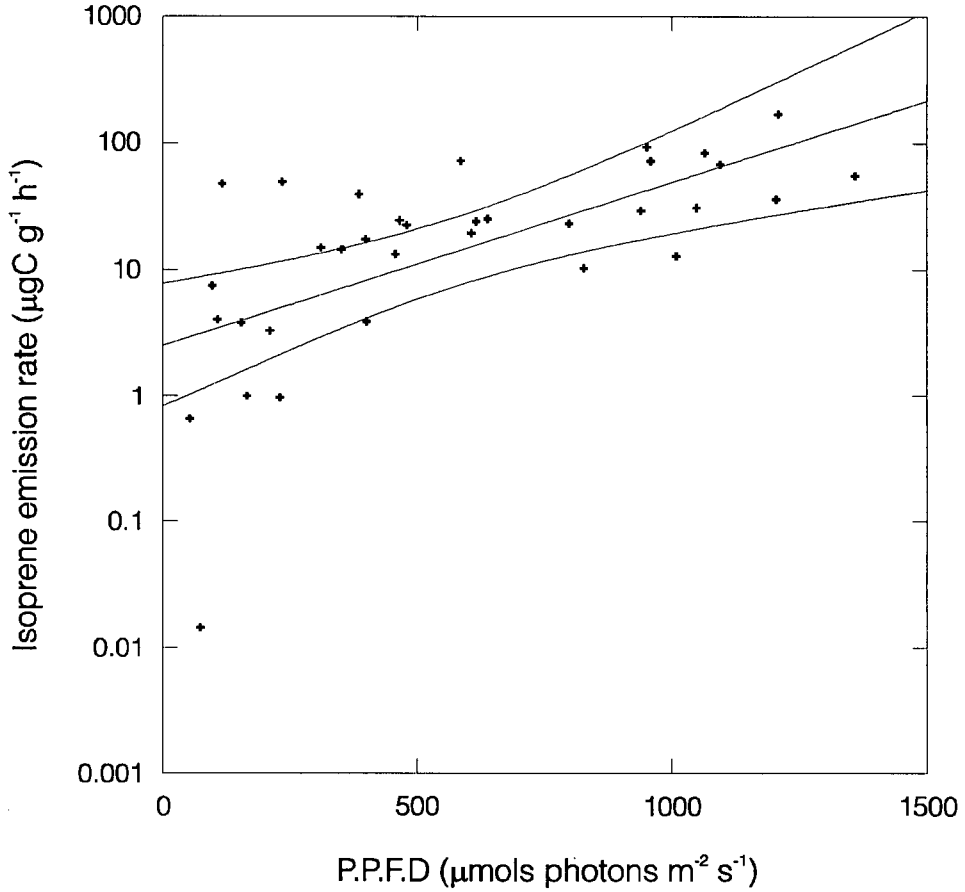

Figure 3-11 Plot of isoprene emission rate from Cottonwood branches vs. photosynthetic photon flux density

Figure 3.12 shows average relative contribution of the three main classes of hydrocarbons to each tree species emissions. Similarly, table 3.2 shows the average six most abundant compounds observed in each tree species emissions along with the percentage of total emissions made up of that compound. Of interest is the fact that ethylbenzene is on average, the most abundant compound from both cedar and Hemlock trees. Again emissions from Cottonwood trees are dominated by isoprene comprising an average of 93.4% of the emissions. The next most abundant compound from Cottonwood only makes up 0.8% of total emissions. All coniferous species show different proportions of the various compounds but none of the three display an exceptionally large proportion of their emissions attributable to one single hydrocarbon as do cottonwoods.

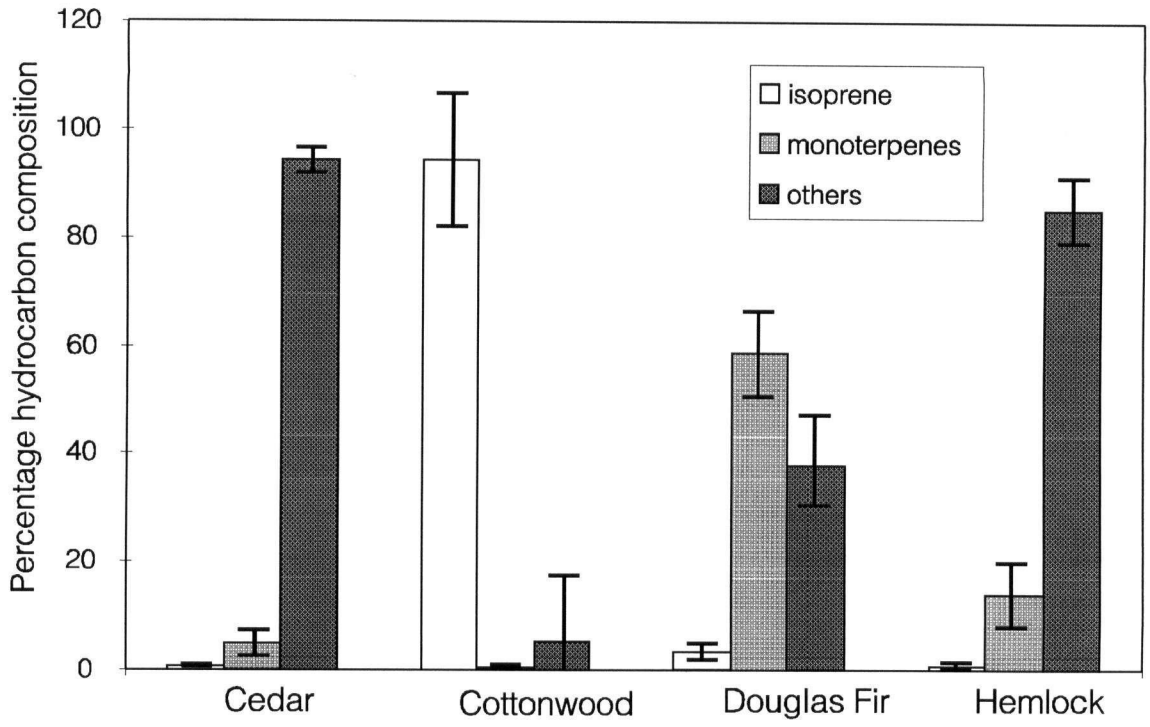

Figure 3-12 Average % composition of branch emissions composed of isoprene, Monoterpenes and other VOC's respectively from four tree species in the Lower Fraser Valley. Error Bars represent ± 1 STDV from mean.

Cedar		Cottonwoods		Douglas fir		Hemlock	
compound	%	compound	%	compound	%	compound	%
ethylbenzene	30.3	isoprene	93.4	α-pinene	43.7	ethylbenzene	32.9
isopropylbenzene	14.1	ethylbenzene	0.8	p-cymene	15.6	α-pinene	10.3
n-butane	8.9	benzaldahyde	0.6	β-pinene	7.5	ethane	7.6
ethane	4.6	ethene	0.4	limonene	6.1	1-pentene	4.4
1-pentene	4.1	ethane	0.4	camphene	4.3	p-xylene	4.1
α-pinene	2.9	limonene	0.3	isoprene	3.4	β-pinene	3.1

Table 3-2: Listing of the six most commonly occuring hydrocarbons (average percent of total emissions by mass) from each tree species.

Figure 3.13 is a plot of percentage of total cottonwood VOC emission comprised of isoprene against temperature inside the cuvette. At lower temperatures, isoprene makes up a smaller proportion of the total hydrocarbon emissions while at a temperature approaching 20°C, almost all of the cottonwood emissions are composed of isoprene.

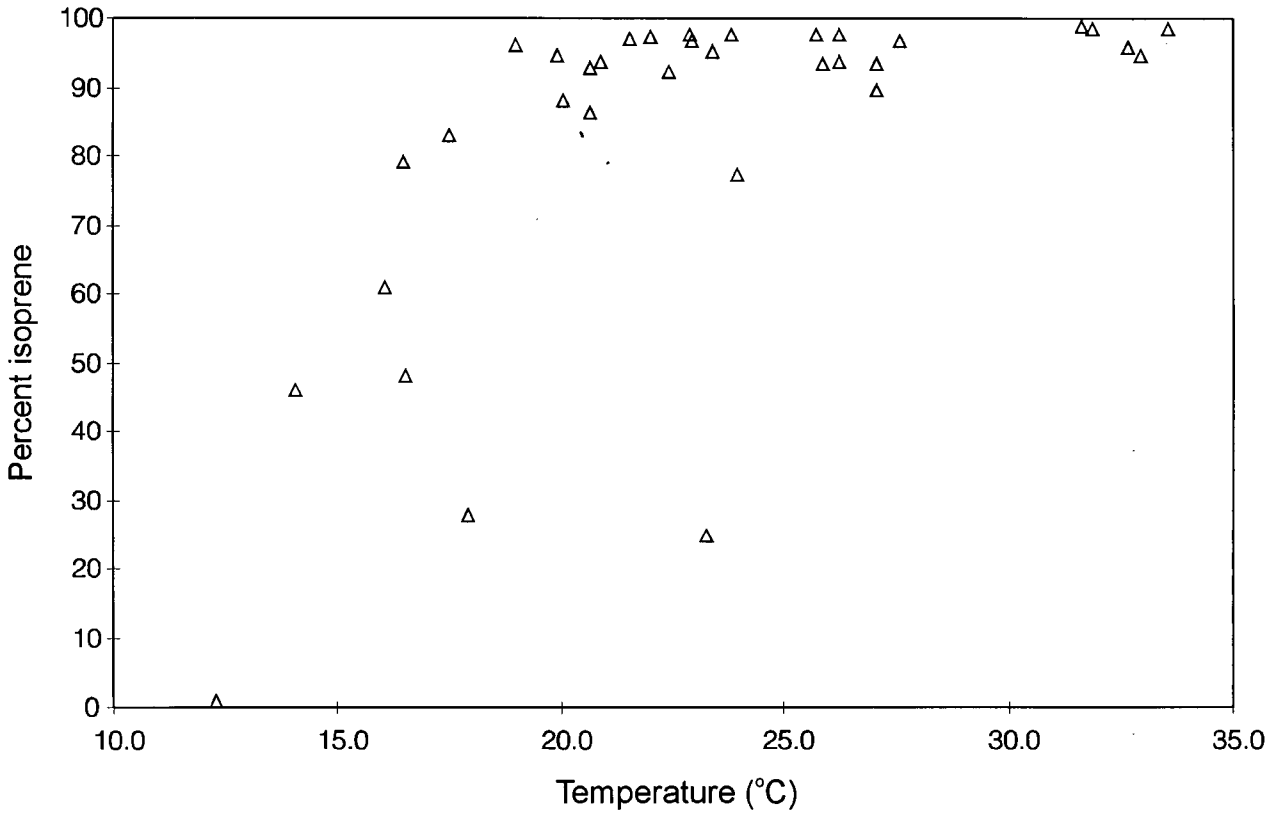

Figure 3-13: Percentage of cottonwood total VOC emissions composed of isoprene as a function of temperature.

3.4 Relationship between CO_2 fixation and isoprene emissions

Figure 3.14 is a plot of the relationship between CO_2 assimilation rate and isoprene emission rate. Carbon used in the formation of isoprene is fixed from a carboxilation mechanism separate and distinct from carbon fixation associated with photosynthesis so it is not possible to draw any conclusions about the pathway of carbon between these cycles. However, these plots do provide a comparison between the four species regarding the amount of energy that is being allocated towards formation of isoprene compared to total energy being assimilated by the fixation of carbon. Again, by virtue of their low emission rates, coniferous trees all show very

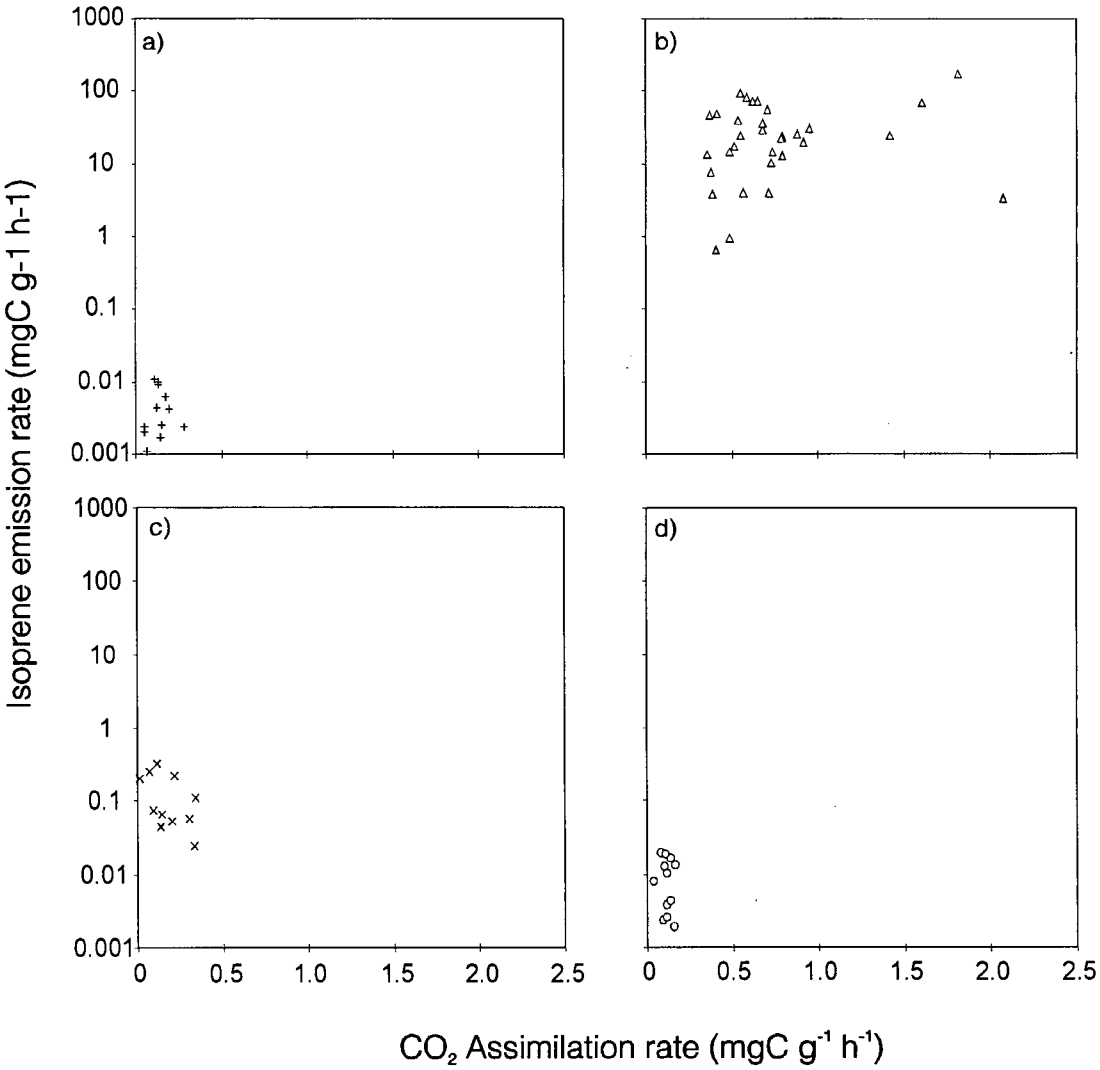

Figure 3-14: Plot of Isoprene emission rate vs. CO_2 assimilation rate for a) Cedar, b)Cottonwood, c) Douglas fir and d) Hemlock.

low ratio of carbon released to carbon assimilated (on a mass basis) with values of 4.0×10^{-6}, 2.2×10^{-4} and 1.0×10^{-5} for Cedar, Douglas fir and Hemlock respectively. As well, these ratios all show little variability from one sample to the next within a species. Cottonwoods trees however release on average almost 5.0×10^{-3} of the total carbon fixed by photosynthesis during emission of isoprene and demonstrates a considerable range about this value. Samples at the upper extremes of temperature and PAR showed the quantity of isoprene emitted approached 1.9×10^{-2} of the total carbon fixed by photosynthesis, slightly less compared to the range of 2.5×10^{-2} to 8.0×10^{-2} observed by Monson and Fall (1989) from Aspen leaves.

3.5 Samples obtained from other species of vegetation

Figure 3.15 shows emission rate of three hydrocarbons sampled with the gas exchange cuvette from four different types of plants commonly found in the Lower Fraser Valley. All of these samples were obtained in temperature and light conditions as close to 30°C and 1000 µmols $m^{-2}s^{-1}$ as possible. Chemical analysis of these samples was conducted either at York University (for canisters) or a GC - FID set up at the University of British Columbia which used a Tenax sample collection system. Only isoprene, α-pinene and limonene were identified since these are generally the most abundant compounds from biogenic emissions and calibration of a GC for identifying a whole spectrum of hydrocarbons requires considerable time and effort. Samples collected using canisters are denoted with a (C) while those collected with Tenax adsorbent are

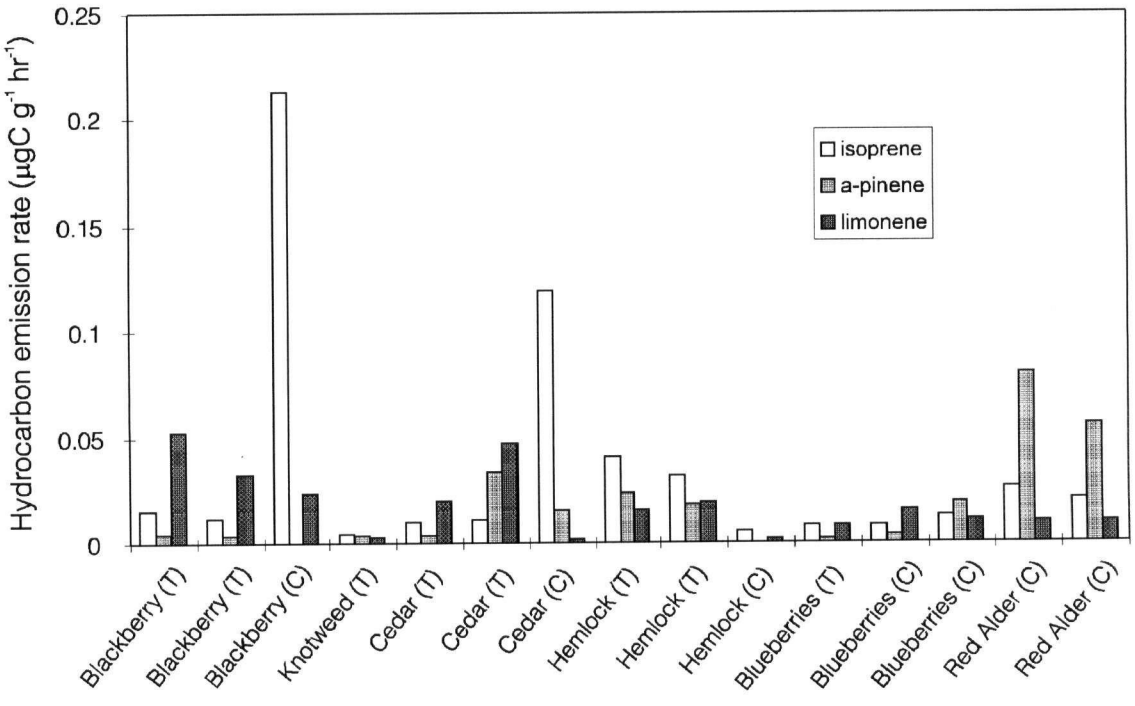

Figure 3-15: Emission rate of three biogenic VOC's from enclosure measurments of other vegetation types in the Lower Fraser Valley. Those followed with a (T) were sampled with a Tenax adsorbant sampling system while those followed with a (C) were sampled into stainless steel canisters.

labeled with a (T). The first three samples on the x-axis were collected from enclosed blackberry branches with the first two using Tenax adsorbent cartridges and the third using a canister. Obviously there is a considerable difference in the flux of isoprene between the two samples. However, the concentrations measured were 0.22, 0.22 and 0.80 ppb isoprene respectively for the two cartridges and the can respectively. These are quite low concentrations so slight differences in accuracy between the two sample collection methods will propagate to large differences in calculated fluxes. Japanese Knotweed obviously had very low emissions of all three hydrocarbons measured. Blueberries, an important agricultural crop in the Lower Fraser Valley area, also demonstrated very low emission rates. Both the Red Alder samples were obtained from canisters and showed remarkable consistency between the two samples. The magnitude of isoprene emissions from Alder is similar to that of the three coniferous trees (i.e. relatively low) while terpene emissions from Alder are also relatively low, similar to all four tree species examined in detail.

Preliminary samples were also obtained from Western Red Cedar and Hemlock trees prior to the detailed field study. Both these vegetation species were sampled twice with a Tenax cartridge and once with a canister. These samples were all obtained during the 9th and 10th of August, almost two weeks before the main sample collection was undertaken (Aug. 23rd for Hemlock and August 31st for Western Red Cedar). Comparison of these preliminary samples with the observed hydrocarbon emissions from figures 3.7 and 3.8 show reasonable agreement. At worst there is a threefold difference between the fluxes measured at the two different times. Most likely this is caused by uncertainties in the differences between the two sample collection techniques but could also be attributed to many confounding factors discussed in the section on error analysis.

4. Discussion

4.1 Field measurements

Some of the observations of this study conform to our expectations based on previous measurements of VOC emissions from plants while for other observations this is not the case. One of the most encouraging results is the well behaved emission response (i.e. increases with temperature with relatively little scatter) of isoprene from all four tree species. Secondly, the magnitude of the emission rate of all four species was quite close to that expected based on other studies (See table 4.1). Even with considerable research into the phenomenon of isoprene emission it still remains that we are not certain as to why plants emit this compound. The possibility that isoprene might be a thermal protection mechanism appears to be the prevailing hypothesis. Coniferous trees generally have relatively small needle shaped leaves and therefore will have very low laminar boundary layer resistance to sensible heat and water vapour flux. This close coupling of needles to the surrounding air will prevent a plant from excessive heating (assuming that air temperature does not go too high) and thus reduce the need for isoprene as a thermal protection mechanism. Examination of geographic distribution of the three coniferous tree species shows that they generally do not occur in very hot dry climates (Elias, 1980) indicating that their morphological characteristics alone could be sufficient to prevent thermal stress in their native habitat. Cottonwoods on the other hand occur over a very wide range of latitudes in western North America ranging from hot arid areas all the way to Alaska. As well, cottonwood leaves are very large compared to coniferous needles, thus presenting a resistance through the laminar boundary layer to the loss of sensible and latent heat. It would therefore be reasonable to hypothesize that isoprene could act as a thermal protection mechanism in this

Tree species	Isoprene	Monoterpenes	Other NMHC	References
Eastern Cottonwood (Black Cottonwood)	25 (112.5)	0 (0.13)	0 (1.32)	Evans et al., 1982
Douglas fir	<0.1 (0.17)	0.5 (0.19)	0 (1.53)	Lamb et al., 1985 Westberg et al, 1982 Guenther et al., 1994
Western Red Cedar	<0.1 (0.007)	0.6 (0.57)	*** (0.02)	Lamb et al, 1985, 1986
Hemlock	<0.1 (0.01)	0.2 (0.13)	*** (0.43)	Lamb et al, 1985, 1986

Table 4-1: Comparison of VOC emission rates from the literature to results from this stydy (in parenthesis). Emission rates have units of $\mu gC\ g^{-1}\ h^{-1}$ and are normalized to 30°C and 1000 $\mu mols\ m^{-2}\ s^{-1}$ PPFD. *** indicates data not available.

species in order to prevent physiological damage and allow cottonwoods to briefly withstand excessively warm temperatures.

It is interesting to note that almost all plants that emit isoprene at high rates are deciduous trees (The Genus *Picea*, (Spruce) being a notable exception) yet the converse is not always true. Trees of the family *Salicaceae* (Genus *Populus* and *Salix*) such as Trembling Aspen (*Populus tremuloides*), Eastern Cottonwood (*Populus deltoides*), Balsam Poplar (*Populus balsamifera L.*) and Weeping Willow (*Salix babylonica*) are all known to be relatively fast growing and very strong emitters of isoprene (Tanner et al., 1992). Other deciduous Genera that display very strong emission rate include *Eucalyptus* (Gum Trees), *Quercus* (Oaks), and *Liquidambar* (sweetgums). However, other tree species that inhabit both hot and cold climates such as Maple (*Acer*) Ash (*Fraxinus*) and Elm (*Ulmus*) generally do not display such high rates of isoprene emission.

Some further comments on the results of the samples from the other common plant species are worth mentioning briefly. The very low rates of isoprene emission from alder are somewhat surprising since it extremely fast growing and deciduous. However, its range is limited to relatively cooler areas so perhaps if isoprene is a heat stress tolerance mechanism, it is not required by this species. Blackberries are another species that grow very rapidly and are quick colonizers of disturbed areas yet again showed very low VOC emission rates. Preliminary observations during the summer of 1994 over cranberry bogs showed very large gradients of isoprene indicating a possible strong areal source. However, during follow up measurements in 1995 the gradients measured were much lower. This could possibly be explained by emissions starting only after a certain stage in development has been achieved. This is similar to the findings of Grinspoon et al., (1991) that isoprene emissions are "switched on" at a certain phenological stage of velvet bean leaves.

Figure 3.14 contains hints of a threshold mechanism regulating isoprene emissions from Cottonwoods. Below approximately 20°C, isoprene is a highly variable proportion of the total emissions ranging from 1 to approximately 80%. Above 20°C however, emissions are composed almost entirely of isoprene since both monoterpenes and the other hydrocarbons display no significant increase in emission rate with increasing temperatures. This close correlation of isoprene emissions with temperature is not proof of any evolutionary purpose or physiological function. However, the observation that the presence of isoprene can delay the onset of damage to membranes coupled with the observed increase in emission at high temperatures presents a strong argument towards isoprene fulfilling a role as a heat stress protection mechanism.

Unlike those of isoprene, emissions of monoterpenes from the four tree species shows a considerable amount of scatter. One possible explanation for the large amount of observed

scatter could be a change in stomatal resistance caused by temperature or humidity variations within the cuvette. As stated in chapter 3 and shown in figure 3.3, temperature inside the cuvette often deviated substantially from outside temperature. Furthermore, cooling and condensation on the bottom of the cuvette could act to lower the absolute humidity and cause the stomates to close (if the branches, exposed to sufficient radiation, remain slightly warmer than the air inside the cuvette). If monoterpene emission is coupled to the transpiration stream as has been suggested by Rasmussen (1972) and Lamb et al., (1985) or is affected by humidity causing changes in cuticular permeability (Tingey et al., 1991) then these changes in humidity could strongly affect monoterpene emission rates while isoprene emissions, being independent of stomatal resistance, would remain independent of humidity. Unfortunately no measurements of relative humidity or stomatal conductance were taken during the field study so it is impossible to say for certain if the status of the stomates are having an effect on emissions. Another possible explanation could be a depletion of the pools of terpenoid compounds within branches because of warm temperatures experienced prior to and during the study period. If production rate of terpenes is less than emission rate and if pool size determines emission rate as suggested by Schindler and Kotzias, (1989) then clearly there will be a decrease in emission rate through time even though temperature remains elevated.

One likely explanation for the extremely high variability of measured monoterpene emission rates is mechanical disturbance of the plants. Although every effort was made to prevent damage to branches during the actual enclosure measurements, it is possible that some did occur which would manifest itself as higher emission rates (see section on error analysis). It is somewhat encouraging to note that the extremely high variability observed in this study is similar

in magnitude to that observed by others both from coniferous and deciduous trees (e.g. see Lamb et al., 1987, Knoerr and Mowry, 1981).

Emissions of compounds in the "other" category would be expected to behave in a manner somewhat similar to monoterpenes. Reasons for this are that both types of VOCs are released from storage sites in the plant and not derived from short term production as is isoprene. The emissions might be coupled to the transpiration of water from the plant or might depend entirely on vapour pressure deficits of the particular compounds. Examination of figure 3.8 and 3.9 shows that there appears to be much less variability in the emissions of other VOCs compared to the monoterpenes even though the magnitude of their emission rates are quite similar. This could be attributed to storage in separate locations within the leaf or to differences in the physical properties of monoterpenes and the other compounds.

4.2 Error Analysis

Estimating the total error in the branch emission calculations requires consideration of all measurement errors of those variables used to calculate branch emission rate. Lamb (1985) conducted a comprehensive analysis of potential errors in flux measurements from both enclosure measurements and flux gradient techniques. This methodology is derived from standard error analysis techniques as described by Bevington and Robinson (1992). The total uncertainty of a measured flux depends on the uncertainty associated with all the different variables measured to calculate that flux. This is expressed in equation 4.1

$$U = \sum_{i=1}^{n} \left| \frac{\partial F}{\partial X} \right| |\Delta X| \qquad (4.1)$$

where $\partial F/\partial X$ is the change in the function F (in this case emission rate) with respect to a single variable X. In this example it is simply the measured flux divided by the value of the variable X. ΔX is the uncertainty associated with the variable X. As a typical example, F is arbitrarily selected to be the emission rate calculated from canister York 054 obtained from a Douglas fir branch. Possible source of error in the calculation of emission rate include uncertainties with flow rates, leaf mass and chemical analysis.

From discussion with the laboratory technicians, errors associated with chemical analysis are estimated to be approximately ± 10% for the total VOC analysis. However, the assumption that background concentration is zero (i.e. that the charcoal filter was 100% effective) can be seen to be untrue in table 4.2. This table shows concentration (in μg of carbon m^{-3}) of the three classes of hydrocarbons from two blank tests (i.e. obtained using the cuvette apparatus but without any branches inside) labeled York 011 and York 394. For comparison, this table lists the arithmetic average concentration observed of the three classes of hydrocarbons from each of the four tree species. In sample York 011 all three classes of VOC occur at very low concentrations indicating

	Concentration						
Compound	York 011	York 394	York 054	Cedar	Cottonwood	Hemlock	Douglas fir
isoprene	0.045	0.063	3.302	0.159	375.971	0.244	1.481
monoterpenes	0.049	0.545	67.124	2.011	2.757	7.399	22.894
others	4.029	63.931	20.066	30.323	39.162	39.068	17.244
total VOC	4.122	64.539	90.492	32.493	417.890	46.711	41.619

Table 4-2: Concentration ($\mu g\ m^{-3}$) of the three classes of hydrocarbons observed in air samples obtained during 1995 field measurements. Canister York 011 and York 394 are samples obtained from a typical Douglas fir (note the relatively high concentration of monoterpenes). The other four samples are the arithmetic average concentration observed from each of the four tree species.

that the charcoal filter is doing an effective job of removing ambient VOCs during collection of that particular sample. Canister York 395 has very low concentrations of isoprene and monoterpenes while the "other" VOCs occur at a moderately high concentration of 64 $\mu gC\ m^{-3}$. In this case the "other" VOCs are dominated by ethylbenzene, isopropylbenzene and n-butane, all of which were not omitted as anthropogenic contaminants during data analysis.

Table 4.3 lists average and maximum concentration of ethylbenzene, isopropylbenezene and n-butane (ppbv) obtained from all branch samples collected on August 31st compared to the blank sample York 395 obtained the same day. Average concentration of ethylbenzene during the branch enclosure measurements on that day is only 9 $\mu gC\ m^{-3}$ compared to the blank test with a concentration of 33 $\mu gC\ m^{-3}$. This strongly suggests that the high concentration of ethylbenzene observed in the blank sample is attributable to short term contamination since the actual branch tests did not reveal high concentrations of ethylbenzene. Isopropylbenzene occurs in the blank canister at a concentration three times greater than that observed during the rest of the day indicating that it too is likely a contaminant. The concentration of n-butane shows general agreement between the blank test and the branch samples collected on this date. From these considerations, it would be reasonable to conclude that the blank sample collected in canister York 394 obtained on August 31st is not representative of background hydrocarbon

	August 31st concentrations		
	ethylbenzene	isopropylbenzene	n - butane
average (branch)	8.979	5.176	2.114
maximum (branch)	15.116	12.929	5.733
blank canister (York 394)	33.276	15.283	2.774

Table 4-3: Comparison of the concentration ($\mu g\ m^{-3}$) of ethylbenzene, isopropylbenzene and n-butane between blank sample (York 394 from table 4.2) and the average and maximum of all other samples collected the same day during sampling of Western Red Cedar.

concentration within the gas exchange system due to the presence of ethylbenzene and isopropylbenzene. Therefore, assuming that the charcoal filter worked consistently, the magnitude of error attributable to contamination of the gas exchange system is the sum of the three compounds detected in canister York 011, and is approximately 4.1 $\mu gC\ m^{-3}$.

The absolute error associated with the analytical balance is only ±0.001 grams, relatively small when considering the mass of the branches (on the order of 5 grams). Calibration sheets provided with the flow controllers state a relative error of 1% during operation. Table 4.4 demonstrates the associated errors of this particular Douglas fir branch emission rate measurement associated with all the uncertainty in the measurement of the variables.

The total relative error associated with this sample is approximately 16%. However, this calculated error was obtained from a Douglas fir tree which does not have a very high absolute emission rate. Since the absolute error is partially fixed (errors from the flow rates, analytical balance and background concentration are all effectively constant from one sample to the next) at higher emission rates the total relative error will decrease. Calculations of the relative error in emission rate from a Cottonwood branch which is emitting VOCs at a high rate indicate that the total relative measurement error will approach 10%. This is however, the relative error for total VOC emissions. The relative error associated with the compounds isoprene and monoterpenes emission calculations is likely to be much less than 15% since the background concentration of (or

Variable	value (X)	error (ΔX)	derivative ∂F/∂X	flux error (μgC g^{-1} h^{-1})	%error
flow rate	0.30 m^3 h^{-1}	0.003 m^{-3} h^{-1}	30.151 μgC g^{-1} m^{-3}	0.091	1.0
chemistry	90.5 μgC m^{-3}	13.171 μgC m^{-3}	0.100 m^{-3} g^{-1} h^{-1}	1.32	14.6
leaf mass	2.99 g	0.010 g	3.027 μgC h^{-1}	0.0300	0.3

Table 4-4: Listing of potential errors from measurements of variables during 1995 field study for total hydrocarbon emission rate (μgC g^{-1} h^{-1}). The hydrocarbon flux F used in this example was a typical Douglas fir sample with a total hydrocarbon emission rate of 9.1 μgC g^{-1} h^{-1}

contamination caused by) isoprene and monoterpenes indicated in table 4.2A for canisters York 011 and York 394 are both very small indicating the total error in their emission rate is likely to be considerably lower.

One of the greatest uncertainties, which cannot be quantified, is the effect of mechanically disturbing or damaging the branches causing an increase in VOC emission rate. Juuti et al (1990) observed a ten to fifty fold increase in emission rate up to two hours after mechanical disturbance. Enclosing a leaf inside a gas exchange cuvette even in a laboratory setting will cause a pulse of monoterpene emissions which can last for a period of hours (Guenther et al., 1991). It is most likely that this uncertainty will cause much more error than all other measurement errors combined. As well, if these branch results are to be used in the compilation of an emission inventory, then uncertainties associated with canopy biomass estimates and profiles of temperature and light through the vegetation canopy as well as vegetation species inventories will also introduce considerably more uncertainty.

It is reasonable to conclude that error associated with measurements of variables such as flow rate, leaf mass, background concentration and chemical analysis (although for the chemical analysis this is based on only two blank tests so it could possibly be an optimistic estimate) is relatively small compared to the variability presented by factors that are very difficult or impossible to control in field studies. These include differences in temperature between the

enclosed branch and the rest of the tree, effects of humidity or plant nutrient status, mechanical disturbance or damage, genetic variability between individuals of the same species and possibly many others. Therefore, if more detailed information concerning hydrocarbon emission rates is desired in the future, minimizing variability caused by these above mentioned factors would prove to be the most worthwhile. It would greatly reduce the uncertainty by compiling an emissions inventory using micrometeorological measurements since this would eliminate the need to measure variable such as specific leaf area and leaf area index, factors which are notoriously difficult to quantify over large areas. However, enclosure studies being a direct measurement of emissions, are quite valuable since they provide a means of independently verifying fluxes measured using other techniques.

4.3 Modelling biogenic VOC emissions.

4.3.1 Isoprene

Owing to the difficulties encountered in measuring biogenic VOC emissions, many researchers have developed numerical simulations in order to model this phenomenon (for examples see Lamb et al., 1993, Guenther et al., 1993, Hov et al, 1983). However, large gaps in our understanding of how these substances are formed and what purpose they serve plants has prevented any mechanistic approach to the problem (Fall, 1991). Rather, empirically derived relations and scaling factors has been the preferred method in the past. Additionally, most observational studies examine scales ranging from leaves to branches with some micrometeorological techniques being able to resolve fluxes at a scale of hundreds of meters. However, heterogeneity in vegetation distribution, both in terms of density and species composition, occurs at many different spatial and temporal scales thus limiting the utility of these models. Furthermore, environmental variables which appear to have an effect on these emissions (temperature, PAR, humidity, wind speed and nutrient/resource availability to mention a few) also display huge amounts of variability at all scales making any regional or larger scale modelling effort very challenging. This section will examine the results obtained in this study and how they compare to a relatively simple model in the literature.

Guenther et al., (1993) hereafter referred to as G93, developed and tested a branch emission model that incorporates our knowledge of mechanistic processes within leaves but still resorts to a degree of empiricism. This model is divided into two separate classes, one for isoprene emissions and another for monoterpene emissions. The isoprene model is similar to that used in equation 1.10. In this case the base emission rate is that observed from a plant at the arbitrarily selected standard of 30°C and a PPFD of 1000 μmols m^{-2} s^{-1}. Temperature and light

correction factors are used to account for changes in emission rate due to changes in these variables and are based on results from empirical gas exchange enclosure studies and knowledge of the mechanisms controlling isoprene production and emission. The light correction factor, C_L is given by:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \qquad (4.2)$$

Where α and C_{L1} are empirical coefficients determined to be 0.0027 and 1.066 respectively. This equation for C_L Yields a Hyperbolic function with a value of 1 at a PPFD of 1000 μmols m^{-2} s^{-2}. The relationship between temperature and isoprene emission rate is somewhat more complicated. At lower temperatures, production of isoprene is assumed to be controlled by the activity of the enzyme isoprene synthase. As temperature increases, the activity, and thus isoprene production rate of this enzyme increases in an exponential manner. However, at higher temperatures the protein structure of the enzyme starts to become heat deactivated (denatured) resulting in a decrease in the concentration of effective binding sites. These two processes can be described by equation 4.3

$$C_T = \frac{\exp \frac{C_{T1}(T - T_s)}{R T_s T}}{1 + \exp \frac{C_{T2}(T - T_m)}{R T_s T}} \qquad (4.3)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), c_{T1} and c_{T2} are empirical coefficients (95000 J mol^{-1} and 230000 J mol^{-1} respectively) obtained from linear best fit procedures using a variety of different plant species. T_s is the standard temperature (303 K) and T_m is another empirical coefficient (314 K). Values for c_{T1} and c_{T2} were found to be almost constant for an assortment of different plant species while T_m changes significantly for different plant species.

Figure 4.1 shows a plot of the modelled normalized isoprene emission rate as a function of both temperature and light conditions for all isoprene emitting plants. The shape clearly shows a very low emission rate at low temperatures and light levels. At very high temperatures the normalized emission rate is observed to decrease because of damage to the biochemical systems that manufacture isoprene. Figure 4.2 shows a plot of the observed isoprene emission rate compared to the modelled rate. In this example every one degree increase in temperature from 10°C is accompanied by an increase of 50 μmols m^{-2} s^{-2} PPFD. This was done for clarity since PAR and temperature are highly correlated in most field measurements and approximates the observed data quite well. The base emission rate was obtained from equation 3.5.

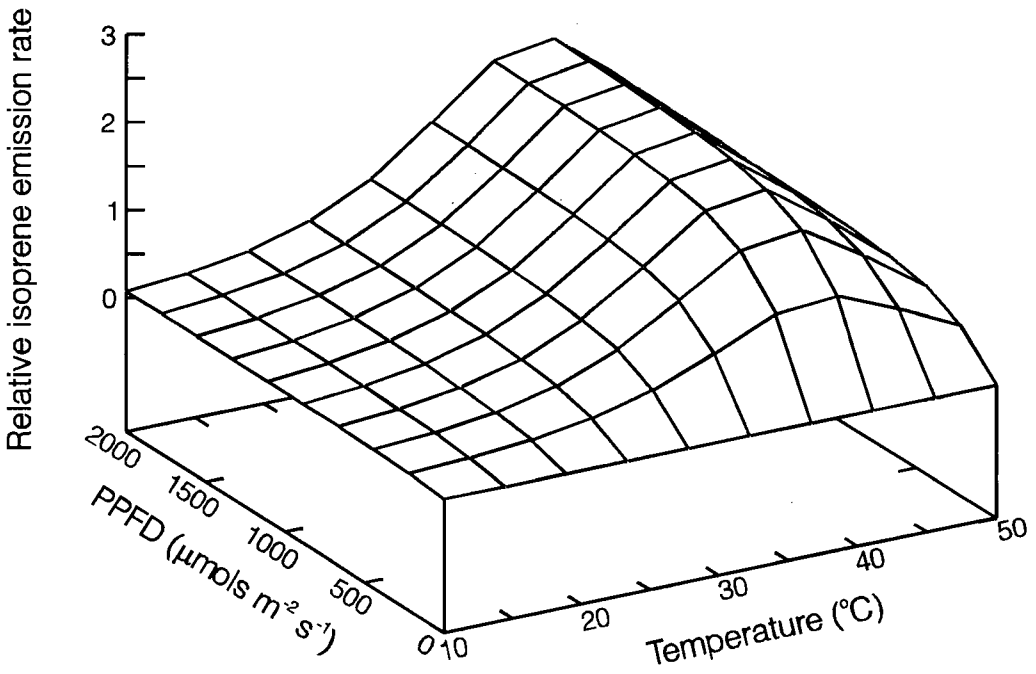

Figure 4-1: Plot of relative isoprene emission rate (nomalized to standard rate) as a function of temperature and PPFD acording to G93 model

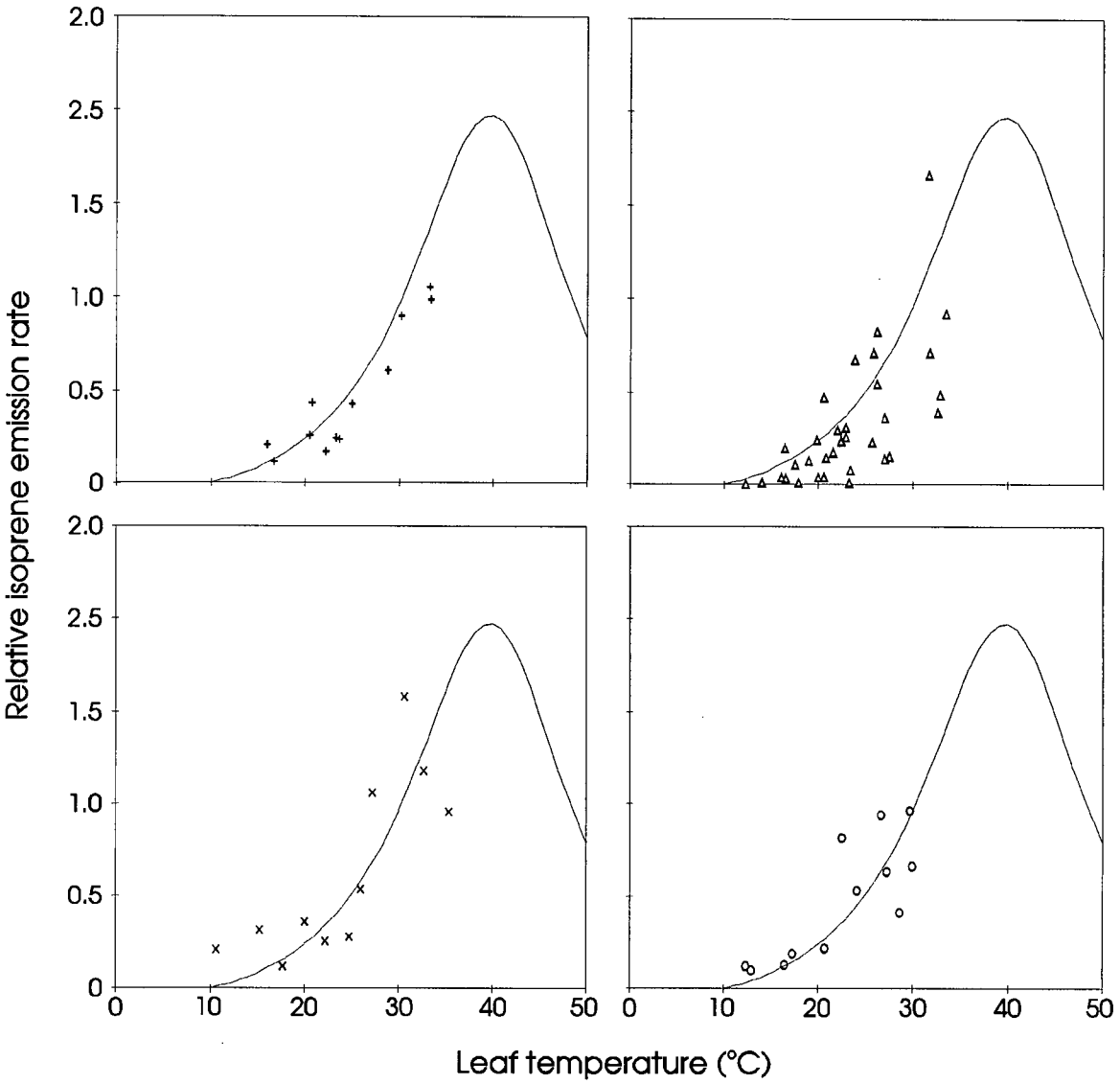

Figure 4-2: Plot of normalized observed isoprene emission rate as a function of temperature from a) Cedar, b) Cottonwood, c) Douglas fir and d) Hemlock. Plotted curve is G93 model

An evaluation of the model performance is provided by NMSE, the normalized mean square error (Equivalent to M in G93):

$$NMSE = \frac{\overline{(E_0 - E_p)}^2}{\overline{E}_0 \overline{E}_p} \qquad (4.4)$$

where E_0 is the observed emission rate, $\overline{E}_0$ is the mean observed emission rate, E_p is the predicted emission rate and $\overline{E}_p$ is the mean predicted emission rate. NMSE depends on three different statistical parameters associated with the relationship between the model and observed results. These are the bias of the variance (F), the bias of magnitude (t) and the strength of the relationship (r). A lower NMSE indicates better model performance. Estimates of the standard deviation of NMSE can also be calculated but this was not done due to the relatively small amount of data collected in this study. Base rates were calculated from the linear regression of the observed emission rates obtained in chapter 3. Values of the NMSE score obtained in this study (Table 4.5) compare favorably to that (0.11) obtained by G93 which compared various models to measurements obtained in the field. Results of laboratory studies as expected show much lower NMSE (G93)

	M score		Pearsons r	
Tree species	G91 model	Linear model	G91 model	Linear model
Western red cedar	0.17	0.05	0.98	0.99
Black Cottonwood	0.33	0.69	0.91	0.91
Coastal Douglas fir	0.33	0.26	0.91	0.93
Coastal Hemlock	0.25	0.20	0.92	0.93

Table 4-5: NMSE and product moment correlation coefficient obtained from comparison of G93 and log linear model to observed data.

Figure 4.3 shows a plot of observed vs. G93 modelled isoprene normalized emission rate for each individual data point collected during the summer of 1995. From examination of figures 4.3 and table 4.4 it is clear that there is a relatively good fit between the normalized model and observed emission rate indicating that our ability to predict the emission rate response of isoprene appear to be reasonably good (at a branch scale). However, for the model to predict absolute emission rate magnitude still requires an estimate of the emission rate at the set of specified standard conditions, information most likely obtained from empirical observations.

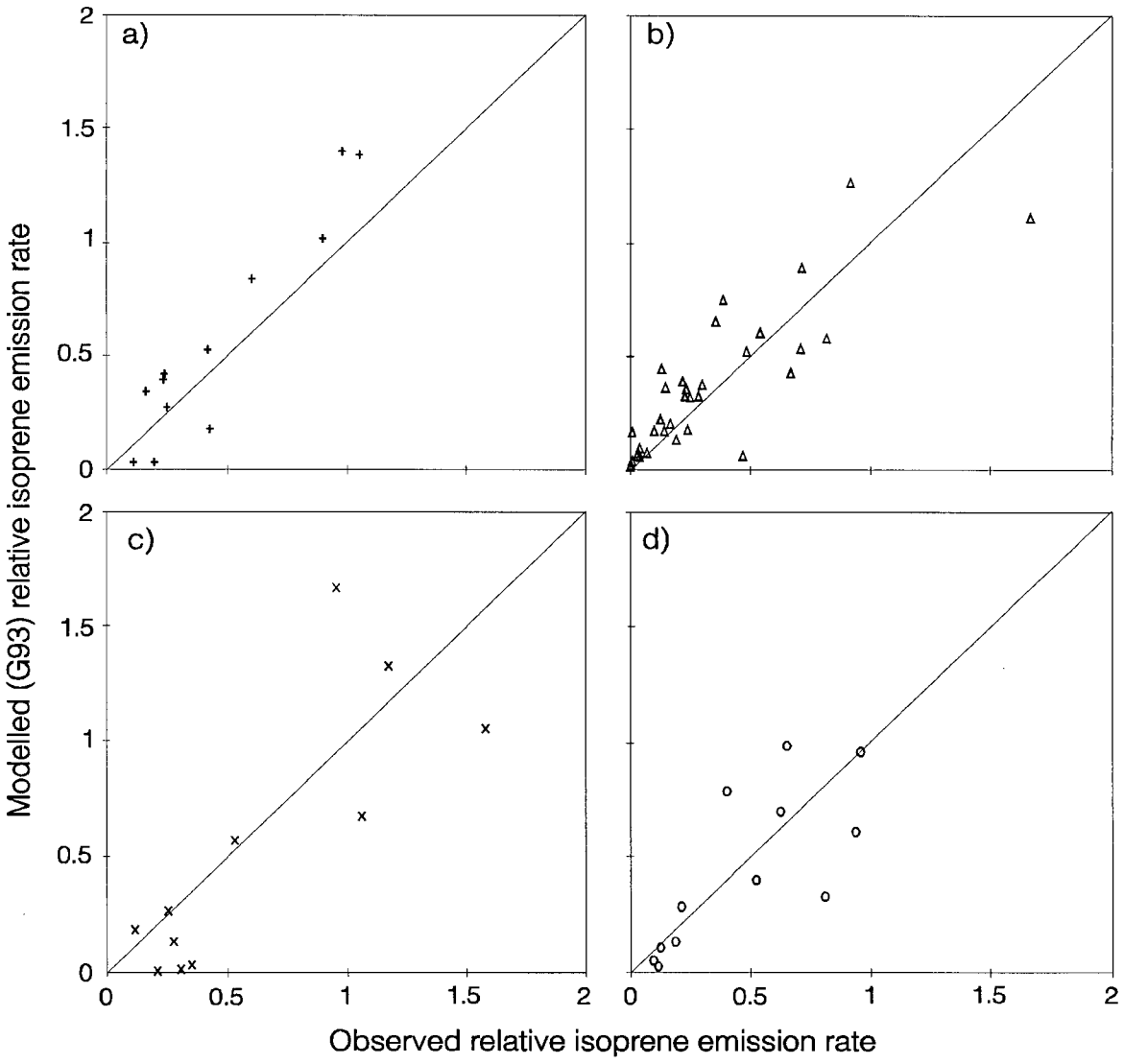

Figure 4-3: Plot of observed vs modelled normalized isoprene emission rate for a) Cedar, b) Cottonwood, c) Douglas fir and d) Hemlock.

The G93 model appears to simulate the emission rate of isoprene reasonably well, however, the higher temperatures where protein damage occurs will rarely happen in the field conditions, especially in a temperate, mid latitude location such as the Lower Fraser Valley. Therefore, results of the G93 model were compared with those expected by the simpler log linear relationship developed from the regression analysis in chapter 3 (hereafter referred to as the log-linear model). Figure 4.4 is a plot of the observed isoprene emission rate compared to the emission rate using this log-linear model. Table 4.5 shows a comparison of the NMSE and r (Pearsons product-moment correlation coefficient) obtained from the G93 model and the log-linear model. Figure 4.6 is a plot of the normalized emission rates calculated from both the log-linear and G93 models. Since both models are essentially the same (i.e. exponential) in the range of temperatures observed, their performance is almost identical. In table 4.5 the high values of r indicate that both models are effective in predicting isoprene emission rate, especially at the range of moderate temperatures encountered in the Lower Fraser Valley region. In areas with higher temperatures and/or severe moisture deficits, thermal denaturing of isoprene synthesizing mechanism could conceivably become an important limitation resulting in better performance of the G93 model compared to a simple log linear model.

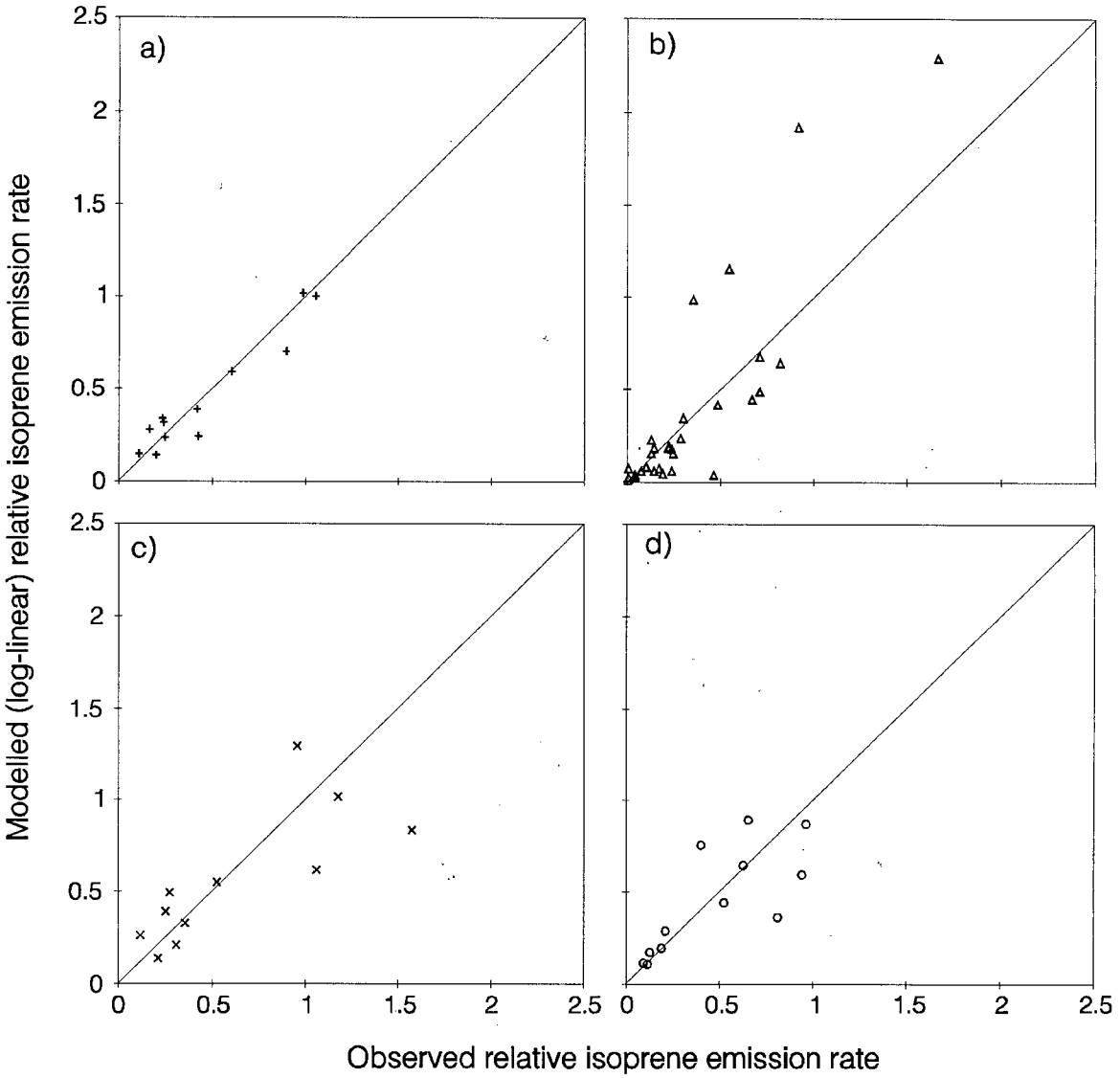

Figure 4-4: Plot of observed vs modelled normalized isoprene emission rate using results from linear regression in chapter 3.

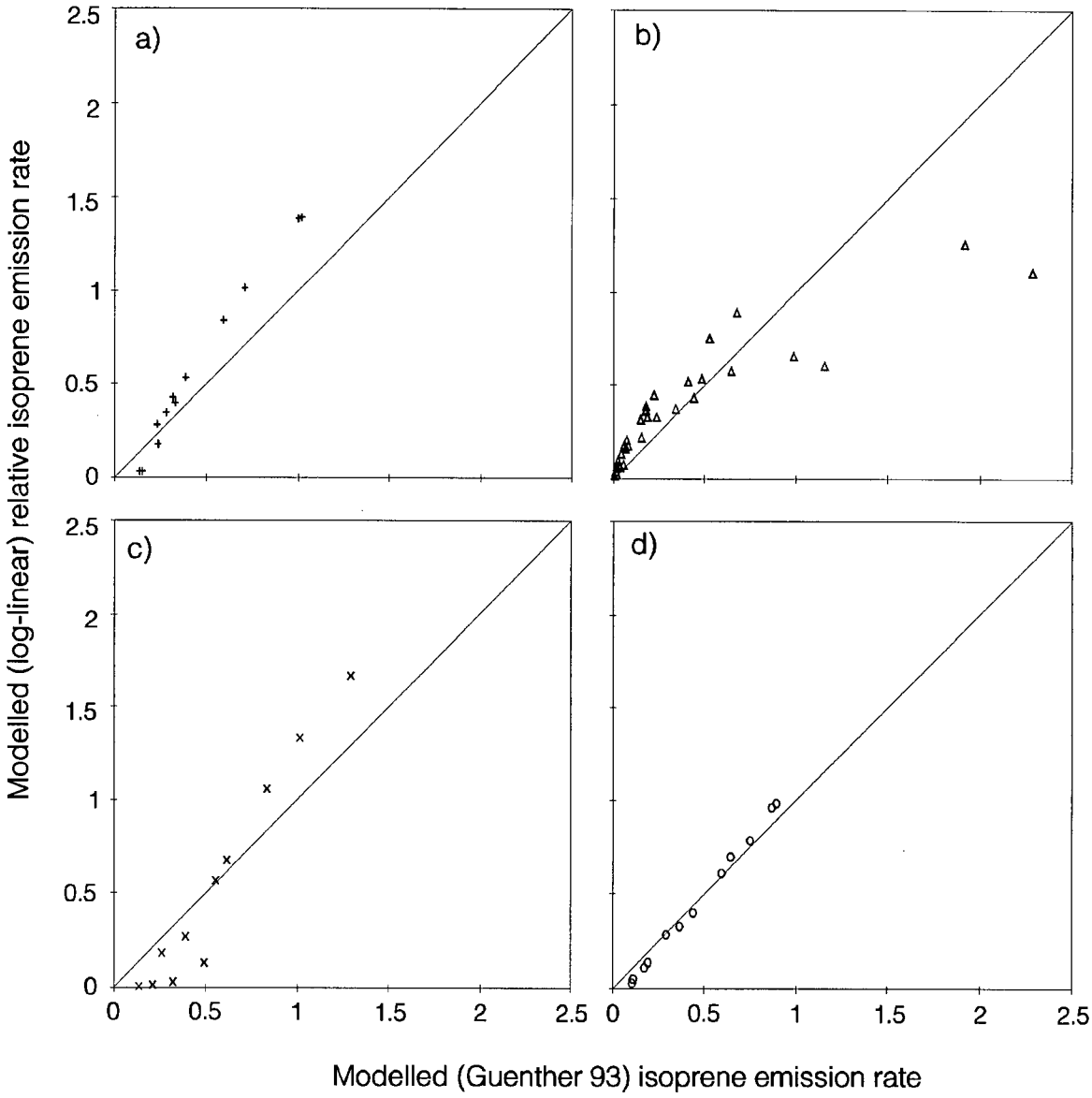

Figure 4-5: Plot of log linear modelled normalized isoprene emission rate vs. that obtained from the G93 model.

4.3.2 Monoterpenes

A model for monoterpene emission rate is different from that of isoprene since emissions are assumed to not be controlled by short term plant physiological responses (except as they change conductance and other physical characteristics of the leaf). A model often used (G93) is given by equation 4.5

$$E_{monoterpene} = M_s \exp(\beta(T - T_s)) \qquad (4.5)$$

Again in this model the base emission rate is determined from empirical data and is usually specific to a single vegetation species (or observations from a particular field study). The value of the parameter β has been tabulated for a wide variety of different terpenoid substances but by virtue of their similar chemical characteristics, 75% of the estimates of β for different monoterpenes have a mean value of $(0.09 \pm 0.025)\ K^{-1}$ (G93).

Figure 4.6 is a plot of observed and modelled normalized monoterpene emission rates from four tree species. The value of β chosen in this example was $0.07\ K^{-1}$ since the common terpenes observed in this study generally have values lower than $0.09\ K^{-1}$. Values in the literature for β are specific to a particular monoterpenoid compounds however, in this particular case, most of the emissions were relatively low and in many cases individual terpenoid compounds were not detected in every sample. For these reasons, the monoterpenes were grouped as one single compound class with a grouped value of β. As was done for the isoprene emission model, the magnitude of the base emission rate was obtained from equation 3.5. Figure 4.7 is a scatterplot of observed vs. modelled normalized emission rate and shows a relatively poor performance of the model compared to observed emission rate. Table 4.6 provides the NMSE and the product moment correlation coefficient obtained from comparison of the observations and the G93 monoterpene model and indicates also a relatively poor performance. Clearly difficulties in the

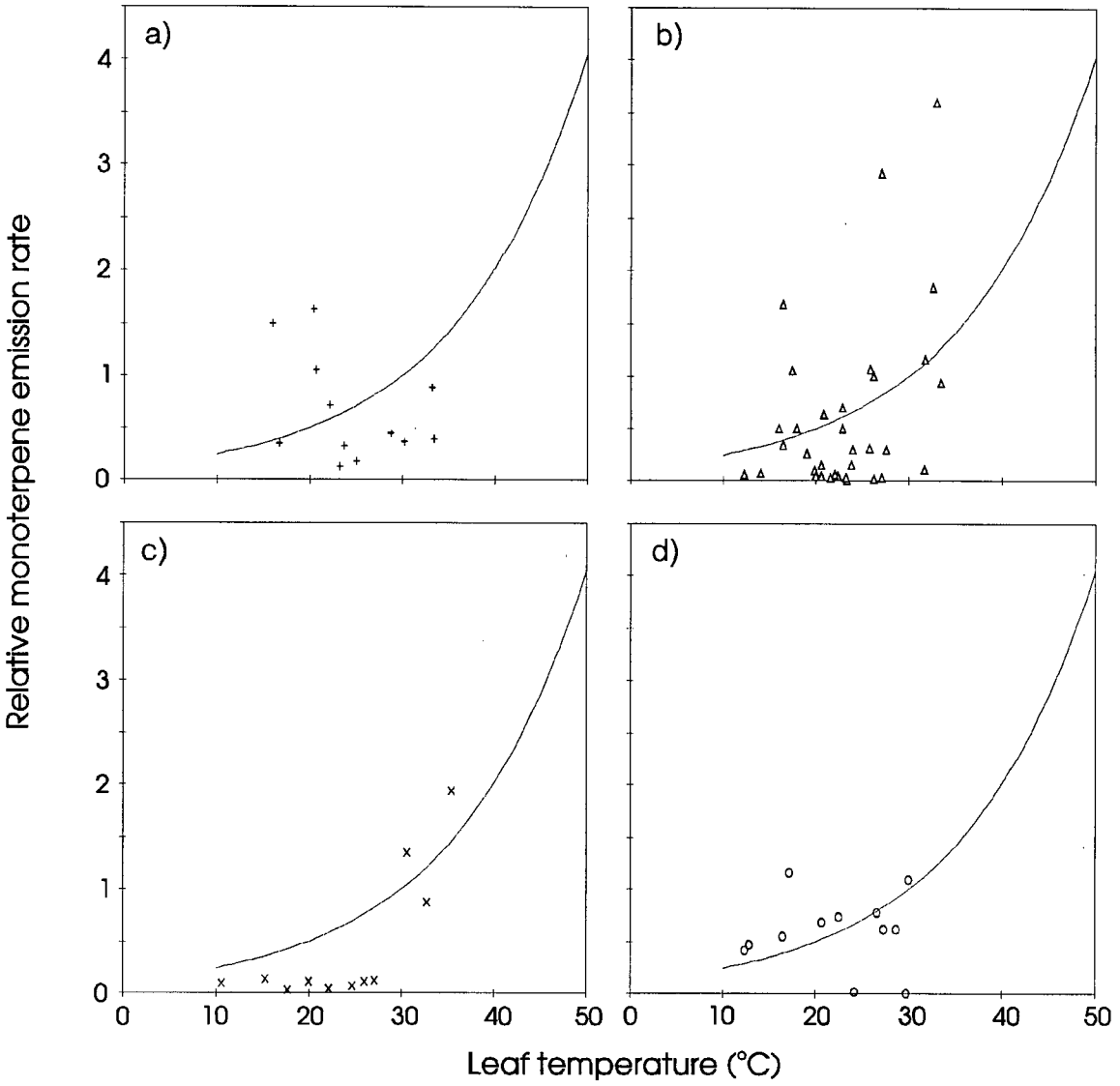

Figure 4-6 Plot of normalized monoterpene emission rate vs. leaf temperature for a) Cedar, b) Cottonwood, c) Douglas fir and d) Hemlock

measurement of monoterpene emission rates from plants still pose a significant obstacle to our understanding of the processes at work.

Tree species	NMSE	R
Western red cedar	0.86	0.68
Black Cottonwood	1.37	0.69
Coastal Douglas fir	0.67	0.83
Coastal Hemlock	0.49	0.80

Table 4-6: NMSE and product moment correlation coefficient obtained from comparison of G93 exponential monoterpene emission model to observed data.

4.4 Comparison of results with other biogenic VOC emission inventories

The emissions measurements obtained in this study will be of considerable value to plant physiologists and others who are interested in VOC emissions from branches. However, these branch emission rates are only part of the overall picture when considering the effect of biogenic VOC emissions on ground level ozone pollution. In order to be useful for air quality applications (primarily emissions inventories), we must be able to extrapolate these branch emission rates to areal fluxes (for example mass of HC m^{-2} h^{-1}). This requires knowledge of the spatial vegetation distribution and species composition of vegetation in a region. It is quite difficult to obtain such information so the best we can do is provide realistic estimates and the uncertainty associated with these values. Fortunately, researchers in forestry, plant physiological ecology and other disciplines have compiled information on canopy characteristics such as leaf area index (LAI - m^2 of vegetation (one side) per m^2 of ground area) and vegetation biomass estimates which are very useful when attempting to extrapolate to larger scales.

Results of this field study can be used to estimate the emission of biogenic VOCs from coniferous forests in the Lower Fraser Valley area and allow comparisons to be made with the airshed emissions inventory (Dunlop et al., 1995) compiled as part of the modelling and measurement studies of the Pacific 93 project. Although only three species were sampled here, these make up a significant proportion of the total coniferous trees in the area. It would also be reasonable to expect those coniferous species not sampled to have emissions that behave in a similar manner even though these rates have not been measured. This is justified by the fact that in the literature almost all coniferous trees studied have consistently low isoprene emission rates. Emissions from deciduous trees were not calculated for two reasons. The first being that cottonwoods, measured in this study, are very strong emitters of isoprene and are likely totally

unrepresentative of other deciduous tree species (for example Alders). Secondly, the areal coverage of deciduous trees in the LFV region is much less compared to the coniferous species and therefore prone to considerable uncertainty.

In order to extrapolate the branch emissions up to areal emissions, estimates of leaf area index and vegetation biomass are required. Korzukhin et al., (1995) conducted a detailed literature review on leaf area indexes and specific leaf areas for the Canadian Forest Service (C.F.S.). As expected, there is a huge range in leaf area indexes observed since this factor will depend on stand density, species composition, tree age and many other site specific factors. However, the projected leaf area index used in the Pacific 93 emissions inventory report for coniferous forests is 5, a reasonable value and is comparable to other coniferous forest studies reviewed in the C.F.S. report. Specific leaf area for coniferous trees ranges from 30 to 60 $cm^2\ g^{-1}$ with 50 being a representative typical value. Table 4.7 provides an estimate and uncertainty in the range of branch emission rates and areal fluxes for the three classes of hydrocarbons as well as a comparison with the Pacific 93 emissions inventory. Branch emission base rates are estimates obtained from analysis of figures 3.7 to 3.9. In order to directly compare the results of this study to that of the Pacific 93 inventory, the flux rate used must be adjusted to account for the total hydrocarbon mass and not just the emissions of carbon, The mass ratio of isoprene to only the carbon atoms in isoprene is 1.133 (same for monoterpenes). This factor was also used for conversion of the "other" compounds to the proper units. Although this is not strictly correct, it is a close approximation and will likely not introduce any significant error.

Compound	Base rate (this study) ($\mu gC\ g^{-1}\ h^{-1}$)	Areal VOC flux (this study) ($\mu g\ m^{-2}\ h^{-1}$)	Pacific 93 flux ($\mu g\ m^{-2}\ h^{-1}$)
isoprene	0.2 ± 0.1	226 ± 113	4091
monoterpenes	1.0 ± 0.5	1133 ± 566	1098
others	1.0 ± 0.5	1133 ± 566	1290

Table 4-7: comparison of areal VOC emission rates for coniferous forests obtained from measurements in this study and those given in the Pacific '93 emissions inventory. Both base emission rates are at 30°C and 1000 μmols photons $m^{-2}\ s^{-1}$. LAI for both calculated fluxes is 5 and the specific leaf area is 50 $cm^2\ g^{-1}$

The most noticeable discrepancy between the two flux estimates occurs for isoprene. The Pacific 93 report provides an areal emission rate almost twenty times that obtained from this study. Furthermore, the base areal isoprene flux calculated in table 4.6 does not consider the attenuation of environmental variables within the plant canopy, rather it assumes a constant temperature of 30°C and 1000 μmols $m^{-2}\ s^{-1}$ of PAR. Both of which will likely decrease considerably from the top of the vegetation canopy and therefore reduce the areal flux estimate considerably. Monson et al. (1995) suggest that isoprene emissions are released mainly from only the uppermost layers of a canopy and might be approximated by multiplying the area based emission rate from a single leaf by the ground area covered by that plant species. Results for the monoterpene and other VOC fluxes show quite good agreement between the two studies.

Although it would be impossible to provide a value of fluxes based only on measurement of Cottonwood emissions, some comments on the Pacific 93 emissions for "mixed trees" are in order. In that emission inventory report, isoprene flux base rate is given as 4897 $\mu g\ m^{-2}\ h^{-1}$. Using the value of leaf area provided (3.7) and a specific leaf area coefficient of 160 $g\ cm^{-2}$ (Korzukhin et al., 1995), an average branch emission rate of 17.3 $\mu gC\ g^{-1}\ h^{-1}$ is obtained. This value places the grouping of "mixed forest" well in the category of high isoprene emitters according to Lamb et al., (1993). In Lamb et al., (1987) a grouped value for deciduous tree

isoprene emission was given as 12.4 μg g^{-1} h^{-1}. However, based on the observation that cottonwood trees are not that common in the Lower Fraser Valley, and knowledge of their emission rates (from figures 3.8 and 3.16), it would seem that isoprene emissions from mixed forests are probably less than the value given in the Pacific 93 report. However, there are a number of deciduous tree species in the region for which no estimate of isoprene are available making any guess of the magnitude of the discrepancy very speculative

5. Conclusions

5.1 Summary

A branch gas exchange cuvette has been designed and employed to measure biogenic VOC emissions from vegetation in the field. This apparatus uses a Pyrex glass enclosure and was used to sample branches up to three meters from the ground. The cuvette uses a continuous flow-through gas exchange system with samples collected in stainless steel canisters which are subsequently analyzed with a GC-FID. Temperature inside the branch enclosure can be modified with a chilled water circulation system. Results of the field program demonstrate that the system appears to operate reasonably well, yielding measured total VOC emission rates ranging from 0.26 to 170 $\mu gC\ g^{-1}\ h^{-1}$. Relative error for a branch emission rate of 9 $\mu gC\ g^{-1}\ h^{-1}$ is estimated to be approximately 15%. However, uncertainties caused by mechanically disturbing a branch are unknown but are likely relatively large compared to measurement uncertainty. Contamination by anthropogenic hydrocarbons was encountered but at sufficiently low concentrations to not obscure the presence of biogenic compounds.

Measurements were obtained from four tree species including Black Cottonwood, Western Red Cedar, Coastal Douglas fir and Coastal Hemlock. The emissions were grouped into three main classes based on plant function and reactivity towards the OH radical (and thus ozone formation). These three classes are isoprene, monoterpenes and others. All four tree species showed a statistically significant exponential increase in isoprene emission rate with temperature with remarkably little scatter. However, isoprene emissions from Cottonwoods displayed a much stronger relationship with temperature as well as showing a much greater magnitude of emissions at all temperatures compared to the three coniferous species. Due to the limited number of

samples, only Cottonwoods showed a statistically significant increase in isoprene emission rate with photosynthetic photon flux density.

Monoterpene emissions from all four of the tree species showed large variability and for three of the four species sampled, failed to show any statistically significant relationship with temperature. However, the magnitude of emissions were generally consistent with those of previous studies. Again it is likely that the relatively small number of samples obtained were the primary cause of the lack of expected positive relationship between monoterpene emission rate and temperature, especially since many laboratory studies do in fact observe this relationship. However, even the Cottonwood samples (n=33) failed to show a positive statistical relationship between emission rate and temperature. Douglas fir trees on the other hand (n=12) demonstrated little scatter and a statistically significant increase in emissions with temperature. Large variability in monoterpene emission rate is likely attributable to the physiological differences between isoprene and monoterpene production and storage in plants. Isoprene is manufactured on a continuous basis during photosynthesis so as long as chloroplasts are operating properly, isoprene emissions should be observed. Monoterpenes on the other hand are stored within the leaf and stem tissues of the plant. Any disturbance will damage these storage sites and cause large amounts of these compounds to be released. It is entirely possible that such minor effects as leaf flutter or branches swaying in the wind are sufficient to cause a significant increase in these emissions.

Emissions of compounds in the "other" category (i.e. excluding isoprene and monoterpenes) behaved in a similar manner to the monoterpenes. Only Douglas fir branches had a statistically significant increase in emissions with temperature.

Emissions of isoprene and monoterpenes from branches were compared to those predicted from a simple model developed by Guenther et al (1993). The model simulating production of

isoprene and is quite similar to models of photosynthesis as discussed in Jones, (1991). This model retains a degree of empiricism since it requires a standard base emission rate to account for the physiological differences between plant species. Comparison of the G93 isoprene emission model with observed results shows relatively good agreement. On the other hand, results of the monoterpene emissions measurements showed remarkably poor agreement with the G93 monoterpene emission model. Again, it is likely that the plants in this study are very sensitive to mechanical disturbance by the act of enclosing a branch thus making any realistic evaluation of monoterpene emissions very difficult.

Extrapolating the results of this study upwards to canopy flux estimates was done in order to provide some insight to the emissions inventory compiled for the Pacific 93 field study. Reasonable values of leaf area index and specific leaf area were used in order to compare the inventory of isoprene, monoterpene and other compounds from coniferous and (to a lesser extent) mixed forests. The estimate for isoprene flux from coniferous forests calculated from this study would be approximately 226 ± 113 $\mu g\ m^{-2}\ h^{-1}$ while that used in the emissions inventory is 4091 $\mu gC\ g^{-1}\ h^{-1}$. Results for monoterpenes and other compounds are in agreement between these observations and the Pacific 93 emissions inventory with both estimates approximately 1000 $\mu gC\ g^{-1}\ h^{-1}$. Since only one deciduous species was extensively sampled in this study, much less can be said about the mixed forest emissions inventory. However, using the values of LAI and SLA from the literature, the average branch emission rate according to the Pacific 93 inventory for a mixed forest is 17.5 $\mu gC\ g^{-1}\ h^{-1}$, well below that of Cottonwoods ($\cong$ 110 $\mu gC\ g^{-1}\ h^{-1}$) but much higher than Alders($\cong$ 0.025 $\mu gC\ g^{-1}\ h^{-1}$). However, Cottonwood trees are not very common in the Lower Fraser Valley and so it would be reasonable to conclude that the mixed forest isoprene emission estimate in the Pacific 93 inventory is also somewhat high.

5.2 Recommendations for future studies

Although the branch emission rates obtained from measurements in this study have considerable uncertainty, most of them are attributable to factors that were not controlled. Future projects examining biogenic VOC emissions should attempt to address these variables. Foremost would be uncertainty caused by disturbing the branch, effects caused by changing the water balance of the enclosed branch, development stage of the vegetation being studied and the long term nutrient budget of the plant.

Other areas which would bring considerable benefit include:

1. Implementation and operation of micrometeorological techniques for measuring biogenic VOC emissions over extensive vegetation canopies. An integrated field program comparing these techniques with enclosure studies would be of great benefit not only in the validation of new techniques such as eddy accumulation but would also improve our confidence in our current emissions inventories. The implementation of models that allow us to scale from a leaf to a canopy require careful consideration (Baldocci, 1989) Incorporating both microclimate based models and photosynthetic / physiological models similar to that proposed by Price and Black, (1989) will likely bring about improvements in our canopy VOC emission estimates.
2. Another source of uncertainty in the compilation of emissions inventories has been the extrapolation of results from the laboratory to the real world. Differences in growth history between laboratory specimens and natural vegetation make this a possible source of significant error. However, if results of this study were replicated in a laboratory setting, this would also decrease the amount of uncertainty in our emissions inventories.
3. Due to the difficulty in obtaining measurements of biogenic VOC emissions, there is a lack of data required for evaluation of emissions models such as that proposed by Guenther et al., (1993) or Fuentes et al., (1995). More information needs to be obtained on emission rates

from commonly occurring plant species in Canadian regions that experience ground level ozone episodes. Currently, results from studies conducted in other areas (mainly the southern United States) are extrapolated to many different regions even though vegetation characteristics as well as short and long term environmental conditions may vary considerably.

4. Comparison of emissions inventories with ambient observations have revealed some very curious results. During the Pacific 93 study, ambient concentrations of isoprene as high as 5 ppb were consistently measured on a river levee at a field site in the Lower Fraser Valley (Biesenthal et al, 1996). The following year at the same location this same high concentrations were observed again. However, ambient sampling in other nearby regions revealed at most approximately 0.5 ppb. (See appendix 3 for an explanation). Clearly there is a large discrepancy between the observed ambient concentrations of isoprene and VOCs and the emission rates observed in this and other studies. By examining the relationships between photochemical oxidation products and VOCs we can better establish likely emission rates and relative contribution to ozone formation.
5. This study has examined only four commonly occurring tree species in the Lower Fraser Valley. However, many various factors including rapid urban expansion, changing patterns of agriculture and possible changes in climate could potentially alter the emissions inventory significantly. Plantations of rapidly growing poplar trees are currently being grown in the eastern portion of the Fraser Valley for low grade pulp. Although the areas involved may be very small, the high emission rates from these species could have an impact on future emissions estimates. Planting non native deciduous trees such as weeping willows in urban and suburban regions could also force us to revise our emission estimates. Relatively slight changes in climate might shift species composition towards plants with significantly different

isoprene emission rates than currently observed (Monson et al., 1995) All of these factors require careful consideration for present and future regional emissions inventories.

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Appendix 1

Measurement of leaf boundary layer resistances.

Flow rate used for dynamic gas exchange enclosure studies must be a compromise between two opposing needs. Chemical analysis increases in accuracy at greater hydrocarbon concentrations which must be accomplished by increasing the residency time (or reducing the flow rate into) in the gas exchange chamber. At lower flow rates however, turbulence within the enclosure will decrease and prevent adequate mixing. Furthermore, the laminar boundary layer resistance (see Monteith and Unsworth 1991 for a review of resistances) as opposed to the physiological response of the leaf will begin to play a greater role in regulating the flux of mass and energy between the leaf and the surroundings. For these reasons, it is important to control the flow rate within the cuvette that minimizes boundary layer resistance of leaves yet has a sufficiently long residency time to facilitate chemical analysis.

Numerous researchers have investigated the relationship between boundary layer resistance and a characteristic size (d) of an object at various wind velocities (u) with wind tunnel studies. Parlange et al., (1970) developed an empirical relationship for boundary layer resistance of flat leaf shaped objects (eqn A1.) using such an empirical approach.

$$r_{bh} = \frac{320}{\beta}\sqrt{\frac{d}{u}} \qquad \text{(A1)}$$

In this case β has a value between 1 and 10 to account for turbulence intensity. Unfortunately, it is impossible to relate the flow rate into a cuvette to flow characteristics such as a linear velocity or turbulence intensity. For this reason, a more direct measurements of boundary layer resistance have been made by measuring gradients and fluxes of evaporating substances from leaf or branch shaped porous objects (e.g. Landsberg et al., 1970). Unfortunately, these studies are all quite technically difficult and are prone to significant errors.

A third method that has been used successfully is to calculate sensible heat flux from an object. Measurement of the energy budget of an object and temperature gradient between it and the surrounding free air allows calculation of laminar boundary layer resistance (r_{bh}) to sensible heat flux (e.g. see Amiro et al, 1984 and Brenner et al., 1995). This study follows the same approach by measuring all important terms of the energy balance of a small heated flat plate inside the cuvette in order to obtain an estimate of the boundary layer resistance of leaf shaped objects to heat. This information can then be used to estimate flow rates that provide sufficient residency times for accurate hydrocarbon measurement while ensuring adequate mixing.

Experimental procedure

The experimental set up is relatively simple. A pump is used to provide air to the gas exchange cuvette (see chapter 2) while the flow rate is controlled with a single 10 SLPM flow controller. The flow controller is regulated with a Campbell 21X datalogger which increases the flow rate from 1 to 10 liters per minute at ten minute intervals. As well, the datalogger monitors air temperature (T_a) and temperature of a small heated plate inside the cuvette (T_p) using fine wire thermocouples. Two thermocouples were used to monitor the air temperature inside the cuvette while four thermocouples were used for the plates. Different combinations of flow rate and nozzle configuration were attempted in order to determine which would provide the lowest boundary layer resistance at the lowest flow rate. Some experiments were also done using a small piece of heated nichrome wire to simulate a coniferous needle.

The energy balance of the plate or needle is provided in equation A2

$$\frac{V^2}{\Omega_p A} = 2\varepsilon_p \sigma T_p^{\,4} - 2\varepsilon_p \sigma T_c^{\,4} + \rho C_p \frac{(T_p - T_c)}{r_{bh}} \qquad \text{(A2)}$$

I II III IV

V is voltage drop across the heated plate or wire, Ω is electrical resistance (ohms) of the heated object and A is surface area of the heated object (m^2). ε_p is emissivity of the heated object (assumed to be 1 since it was an flexible plastic surface). σ is the Stefan Boltzmann constant (5.67×10^8 W m^{-2} K^{-4}). ρ is density of air at T_a (kg m^{-3}) and C_p is the specific heat capacity of air (J k^{-1} kg^{-1}). Term I in this equation represents the input of electrical energy into the heated object. Term II is the loss of energy through longwave radiation while term III is the gain of energy from long wave radiation from the walls of the cuvette (assumed to be at the same temperature as the air inside the cuvette). Experiments were all done in the dark in order to neglect short wave radiation. Term IV is simply the loss of sensible heat from the plate due to forced convection from the flowing air. Knowledge of these terms allow r_{bh} to then be calculated at the various flow rates and nozzle configurations.

Observations and discussion

Figure A1 a shows a plot of boundary layer resistance versus flow rate for three different plate positions within the cuvette. All of the plates show a decrease in resistance as would be expected since flow rate and turbulence intensity within the cuvette is increasing. The plate located in the middle of the cuvette (indicated by the squares) has a slightly greater boundary layer resistance than the other two plate positions adjacent to or on the opposite side of the cuvette from the air nozzle. It is suspected that this is caused by a circulation pattern being initiated which leaves a slightly quiescent zone away from the walls of the cuvette.

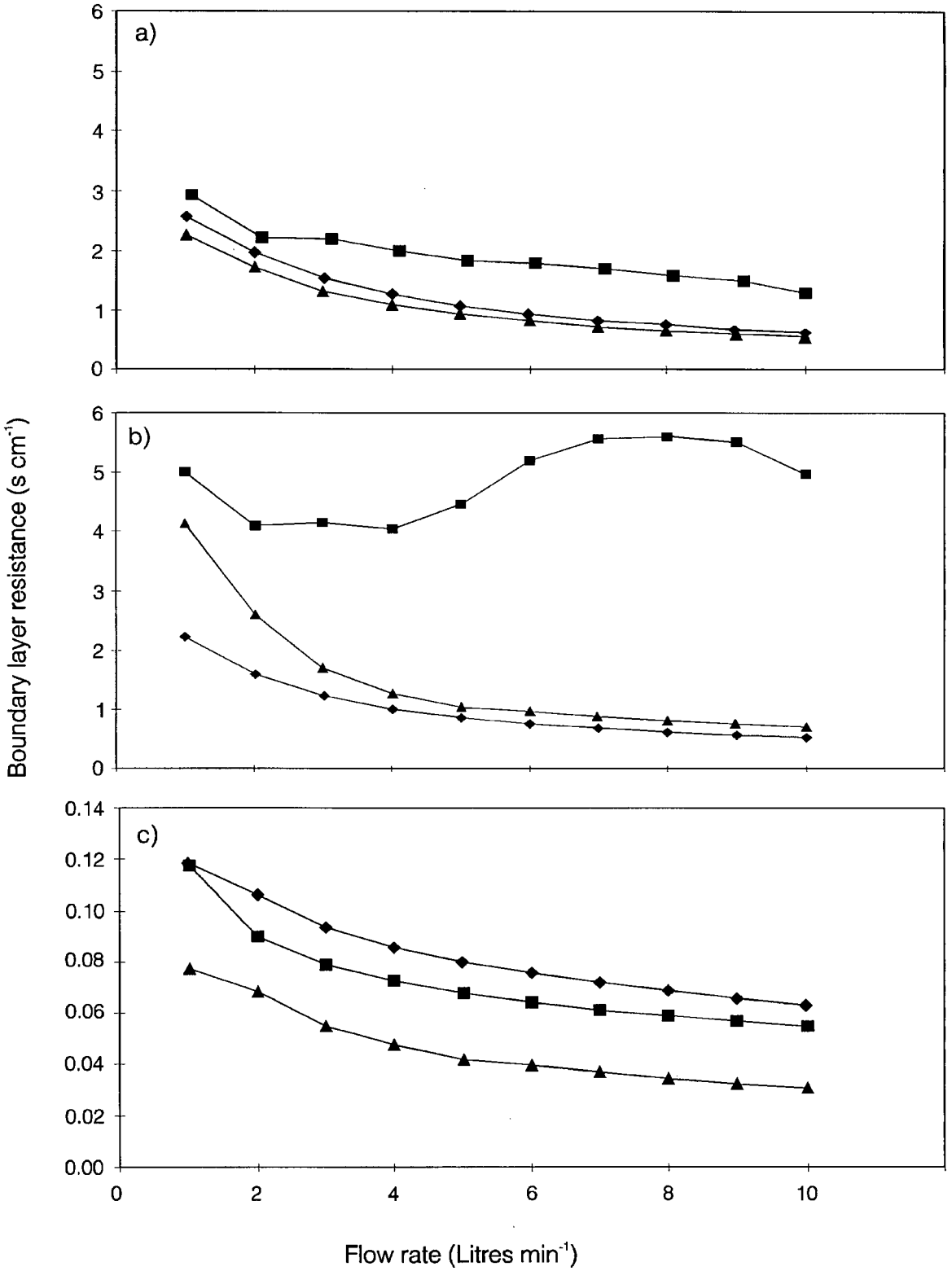

Figure A1. Boundary layer resistance to heat as a function of flow rate inside cuvette for a) flat plate with a single nozzle b)flat plate with two nozzles and c) heated wire with one nozzle.

Figure A1 b is a plot of values of r_{bh} at different flow rates but in this case the configuration of the output nozzle was varied while the heated plate was oriented horizontally in the center of the cuvette. The first experiment used a single nozzle pointed in a downward direction in the cuvette (plotted as squares). This trial shows an initial decrease followed by a very noticeable increase in r_{bh}. Again a likely explanation is the initiation of a circulation pattern inside the cuvette which left a relatively quiescent area in the center of the cuvette volume. Trial 2 (triangles) used two nozzles, one pointing downwards and one pointing directly across the spherical cuvette. The two nozzles cause sufficient turbulence and interference with each other so that no circulation pattern is achieved. Trial 3 (diamonds) was simply one nozzle directed straight across the centerline of the cuvette to the plate.

The third experiment involved measuring the boundary layer resistance to heat of a small heated nichrome wire (diameter $\approx$1 mm) located at various positions within the cuvette (see figure A1 c). Although there was a slight difference in r_{bh} measured for different positions, the absolute value of r_{bh} was approximately one order of magnitude less for a thin needle shaped object compared to a flat leaf shaped object.

Comparison of these results to other researchers work is almost impossible because of the unique combination of flow rates, residency times and enclosure shapes. However, the relationship between flow rate and r_{bh} observed in this study is qualitatively similar to that of others (eg see Landsberg et al., 1970, Fuentes et al., 1992, Brenner et al, 1995). For this study the bottom portion of the cuvette will be chilled in order to provide cooling during the branch experiments. In order for this cooling to be effective, air near the bottom of the cuvette should be mixed by having a nozzle pointed downwards. From figure A1 b the configuration of two nozzles, one pointed downwards while one is pointed towards the heated plate, provides relatively low values of boundary layer resistance and mixing within the cuvette. At a flow rate of five liters

per minute the value of r_{bh} is close to 1 s cm^{-1} while the lowest stomatal resistances encountered for coniferous trees are generally on the order of 2 to 10 s cm^{-1} (Jones, 1992). It should be noted these resistances are for single isolated leaves or needles. Large numbers of leaves or needles inside the cuvette will provide a degree of sheltering which will increase the value of r_{bh}. In generally however, if care is taken to not crowd the branch inside the cuvette, at a flow rate approaching 5 litres min^{-1} the physiological response of the plant will be the main control on emissions of trace gasses while the flow characteristics of the enclosure will not play a significant role in limiting fluxes from the branch.

Appendix 2

Listing of compounds observed during chemical analysis and their retention times

Compound	Retention Time (min)
ethylene/acetylene	7.793
ethane	7.909
propene	8.629
propane	8.731
propyne	9.298
isobutane	10.275
iso-butene	11.199
1,3-butadiene	11.333
n-butane	11.542
t-2-butene	12.01
2,2-dimethylpropane	12.095
1-butyne	12.304
c-2-butene	12.638
3-methyl-1-butene	14.205
2-methylbutane	15.117
1-pentene	15.958
2-methyl-1-butene	16.358
n-pentane	16.583
isoprene	16.833
t-2-pentene	17.067
c-2-pentene	17.49
2-methyl-2-butene	17.758
2,2-dimethyl-butane	18.57
cyclopentene	19.543
4-methyl-1-pentene	19.856
3-methyl-1-pentene	19.906
cyclopentane	20.164
2,3-dimethyl-butane	20.338
c-4-methyl-2-pentene	20.558
2-methylpentane	20.63
t-4-meth-2-pentene	20.746
3-methylpentane	21.443
2-ethyl-1-butene	21.764
1-hexene	21.822
n-hexane	22.474
c-3-hexene	22.665
t-2-hexene	22.772
c-3-methyl-2-pentene	23.066
c-2-hexene	23.296
t-3-methyl-2-pentene	23.649
2,2-dimethylpentane	23.855
methylcyclopentane	23.949
2,4-dimethylpentane	24.225
2,2,3-trimethylbutane	24.486
benzene	25.324

cyclohexane	25.822
2-methylhexane	26.359
2,3-dimethylpentane	26.447
3-methylhexane	26.842
1-heptene/2,4,4-trimethylpentane	27.59
t-3-heptene	28.068
heptane	28.173
t-2/c-3-heptene	28.432
c-2-heptene	28.878
methylcyclohexane	29.311
2,2-dimethylhexane	29.382
2,5-dimethylhexane	29.915
2,4-dimethylhexane	30.028
2,3,4-trimethylpentane	30.897
toluene	31.152
2-methylheptane	31.711
4-methylheptane	31.795
3-methylheptane	32.108
c-1,3-dimethylcyclohexane	32.318
t-1,4-dimethylcyclohexane	32.42
2,2,5-trimethylhexane	32.676
1-octene	32.852
t-1,2/c-1,4-dimethylcyclohexane	33.347
n-octane	33.43
t-2-octene	33.603
t-1,3-dimethylcyclohexane	33.695
c-2-octene	34.033
c-1,2-dimethylcyclohexane	34.896
ethylbenzene	35.972
m-xylene	36.377
p-xylene	36.43
styrene	37.251
o-xylene	37.495
1-nonene	37.732
n-nonane	38.258
iso-propylbenzene	39.009
benzaldehyde	39.875
alpha-pinene	39.985
3,6-dimethyloctane	40.173
n-propylbenzene	40.361
camphene	40.646
3-ethyltoluene	40.675
4-ethyltoluene	40.779
1,3,5-trimethylbenzene	41.018
2-ethyltoluene	41.498
beta-pinene	41.846
myrcene	42.026
1,2,4-trimethylbenzene	42.139
t-butylbenzene	42.224
1-decene	42.582
n-decane	42.712

2-carene	42.805
iso-butylbenzene	42.833
sec-butylbenzene	42.955
3-carene	43.294
alpha-terpinene	43.367
1,2,3-trimethylbenzene	43.39
para-cymene	43.506
limonene / indan	43.937
1,3-diethylbenzene	44.476
1,4-diethylbenzene	44.759
n-butylbenzene	44.816
gamma-terpinene/1,2-diethylbenzene	45.024
undecane	46.83
napthalene	49.1
hexylbenzene	55.475

Appendix 3

Results of ambient sampling

Ambient air samples were collected during the summer of 1995 from various locations near the branch emission study sites. These ambient samples were obtained using stainless steel pumps, a flow controller and a short length of Teflon tubing and were stored in the stainless steel canisters described in chapter 2. The air intake was located between 1.5 and 2 meters from the ground and away from any obvious source of hydrocarbons (e.g. roads, vehicles etc.). Since very little of the gas exchange system was used for these samples, there is virtually no chance of contamination by substances desorbing from surfaces. However, one concern when using this type of sampling arrangement is the possibility that the intake will be in the plume of a very strong (but unknown) local source of biogenic hydrocarbons and be unrepresentative of the "average" hydrocarbon composition of the area. For this reason, the samples were usually located in clearings 10 to 15 meters away from the nearest vegetation canopy.

Table A3.1 shows the location, date and time of collection of each ambient sample as well as a listing of the more common hydrocarbons observed. Data was not grouped into paraffins, olefins and aromatics as was done in Arnts and Meeks (1981). All five samples show a total VOC concentration of approximately 20 to 50 PPBC and are comparable in concentration to relatively clean unpolluted air obtained from the Great Smokey mountains in late September by Arnts and Meeks (1981). They also show much lower VOC concentrations than those obtained from urbanized or suburban air samples in the Tulsa Oklahoma region (approximately 300 to 500 PPBC). Comparison of the relative isoprene concentration of samples collected in this study with those collected by Arnts and Meeks (1981) also show considerable differences. Percentage of isoprene observed in this study is much higher than that observed for urban air from Tulsa and is much lower than that observed from the Great Smokey mountains. The most likely explanation is

high isoprene emission rates in the great smokey mountains from extensive deciduous vegetation while the air samples collected from the Tulsa region are dominated by anthropogenic compounds.

Khalil and Rasmussen (1992) also conducted a study on vegetation fluxes and ambient concentrations in the state of Louisiana. Their ambient samples showed approximately two to five times greater total VOC concentrations than those collected in this study. This is not surprising considering 1) the high emission rates of isoprene from vegetation in southern areas and 2) the relatively small fetch in this study from the sampling sites to the shoreline of the Georgia Straight. Isoprene concentrations observed from samples in the state of Louisiana are approxiamtely 90 PPBC, considerably higher than any isoprene concentration observed in the Lower Fraser Valley. However, these values are not unreasonable when considering the high emission rate of isoprene from deciduous vegetation in a warm climate

location	Cottonwood	Cottonwood	Douglas Fir	Cedar	Hemlock
date	June 22 1995	June 22 1995	July 6 1996	Aug. 31 1995	Aug. 23 1996
time	9:05	17:15	15:30	16:15	14:40
a-pinene	2.002	0.274	0.852	1.960	3.890
b-pinene	0.119	0.385	0.075	2.130	0.000
ethylbenzene	0.455	0.283	0.286	0.439	5.328
isopropylbenzene	0.000	0.000	0.000	0.000	0.336
isoprene	0.554	0.521	0.313	0.000	0.393
limonene	0.000	0.123	0.128	1.320	0.000
n-butane	1.181	0.891	2.096	0.170	3.740
propane	0.000	0.000	2.136	0.158	0.456
propene	0.000	0.000	0.585	0.087	0.507
toluene	9.705	1.911	6.065	0.000	3.129
Σ others	15.942	15.918	18.728	39.142	26.143
Σ total	29.958	20.306	31.264	45.407	43.922
% isoprene	1.850	2.564	1.001	0.000	0.895

Table A3 1: Concentration of hydrocarbons (PPBC) obtained from various ambient samples collected near summer 1995 field sites

In three of the five air samples observed in this study toluene occurred at relatively high concentrations indicating a possible anthropogenic source nearby. The three coniferous ambient samples were all collected at almost the exact same location and demonstrate a slightly higher total VOC concentrations compared to the samples collected near the cottonwood grove. This difference could be attributed to the presence of Southwest Marine Drive west of the coniferous sample site or from a large university research facility nearby.

Another very interesting result obtained from ambient sampling was a very high concentration observed at a rural agricultural site located on the levee of the Pitt river. This location was used extensively during the Pacific 93 field campaign and during that field study high concentrations of isoprene were consistently observed. The following year an ambient grab sample measured 25 PPBC of isoprene, again an extremely high value compared to normal atmospheric concentrations downwind of biogenic sources. Upwind from the sampling site was a grassy wet meadow while approximately 500 meters away was a stand of cottonwood trees. However, measurements obtained from within a cottonwood canopy in still warm conditions yielded a maximum isoprene concentration of 10 PPBC. During the summer of 1995 measurements were again taken from the area, however, at this time the grassy meadow was bulldozed as was essentially exposed earth and stubble. The concentration observed at this time was negligible. These observations lead to two possible conclusions. The first is that there was some temporarily variable strong anthropogenic source of isoprene upwind of the site causing the high isoprene concentrations. Attempts to isolate a possible anthropogenic source were unsuccessful. The second possibility is that some of the unidentified plant species in the meadow were very strong sources of isoprene.

In summary, the ambient concentrations observed from these samples are in general agreement with previous studies considering local effects and regional sources of VOCs near the

University Endowment lands. Local sources of anthropogenic hydrocarbons are likely the main contributing factors to the high concentrations of toluene, propane and ethylbenzene observed. The concentrations of the biogenic hydrocarbon α-pinene is quite close to that observed by Khalil and Rasmussen (1992) while the concentration of isoprene is significantly lower in this study. This is most likely due to variations in isoprene source strength associated with different vegetation types. However, there appears to be an extremely high amount of variability when considering the source strength from vegetation and it is quite possible to discover more plants which are strong isoprene emitters.